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(71)Applicant : TORAY DOW CORNING SILICONE CO LTD
(72)Inventor : MATSUDA YOSHIHARU
TSUTSUMI HIROMORI
ASAI HIROYUKI
NAKAMURA TAKASHI

(54) LITHIUM BATTERY

(57)Abstract:
PURPOSE: To stabilize voltage and current and improve reliability by forming an electrolyte from a specified high molecular copolymer cross-linked body in which an electrolyte is connected to a silicon atom through a hydrocarbon group.
CONSTITUTION: In a lithium battery in which negative and positive electrodes having lithium metal, a lithium alloy or a lithium inserting type carbon as active materials are constituted through an electrolyte, the electrolyte is a high molecular copolymer cross-linked material consisting of a high molecular compound containing a polyorganosiloxane chain containing a lithium carboxylate group represented by the formula I in which the electrolyte is connected to a silicon atom through a hydrocarbon group and a polyoxyalkylene chain. The kind, form, and cross-linking density of the high molecular compound are not particularly limited.

$$-COO-Li^{+}$$

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(71)出願人　000110077
東レ・ダウコーニング・シリコーン株式会社
東京都中央区日本橋室町2丁目3番16号

(72)発明者　松田　好晴
山口県宇部市南小羽山町1丁目11番10号

(72)発明者　堤　宏守
山口県宇部市野中2丁目1番18－8号

(72)発明者　浅井　博之
千葉県市原市桜台1丁目21番5号

(72)発明者　中村　隆司
千葉県市原市有秋台西1丁目6番地

(54)【発明の名称】　リチウム電池

(57)【要約】
【目的】　安定した電圧、電流を与える全固体リチウム電池を提供する。
【構成】　金属リチウム、リチウム合金もしくはリチウム挿入型炭素を活物質とする負極と、正極とが電解質を介して構成されているリチウム電池において、前記電解質が、炭化水素基を介してケイ素原子に結合した式、－COO$^-$Li$^+$　で示されるリチウムカルボキシレート基を含有するポリオルガノシロキサン鎖とポリオキシアルキレン鎖含有高分子化合物とから構成された高分子共重合体架橋物からなることを特徴とするリチウム電池。

【特許請求の範囲】

【請求項１】 金属リチウム、リチウム合金もしくはリチウム挿入型炭素を活物質とする負極と、正極とが電解質を介して構成されているリチウム電池において、前記電解質が、炭化水素基を介してケイ素原子に結合した式，$-COO^{-}Li^{+}$ で示されるリチウムカルボキシレート基を含有するポリオルガノシロキサン鎖とポリオキシアルキレン鎖含有高分子化合物とから構成された高分子共重合体架橋物からなることを特徴とするリチウム電池。

【請求項２】 高分子共重合体架橋物が、(A)１分子中に少なくとも２個のカルボキシル基含有炭化水素基を有するポリオルガノシロキサン、(B)１分子中に少なくとも２個の水酸基を有するポリオキシアルキレン鎖含有高分子化合物、および(C)リチウム金属原子を含むアルカリ化合物からなる混合物を脱水縮合反応により硬化せしめることにより製造されたものである請求項１記載のリチウム電池。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明はリチウム電池、詳しくは全固体で安定した電圧、電流を与えるリチウム電池に関する。

【0002】

【従来の技術および発明が解決しようとする課題】近年，リチウム電池はマイクロエレクトロニクスの発展に伴い，高性能化，小形化，薄型化が一段と進んでいる。かかるリチウム電池においては負極，正極の材料および形態の改良もさることながら、それに組み込まれる電解質の改良が要求されており，とりわけ固体化、高柔軟性，高成形加工性を与える意味で固体電解質が重要になってきている。さらに、高イオン伝導性、高リチウムイオン輸率、高信頼性、耐湿性等種々の高度特性が要求されている。従来，このような電解質としては、高分子樹脂マトリックスにリチウム塩を溶解，分散させた固体電解質材料等が知られている。中でもポリオルガノシロキサン鎖とポリエチレンオキシド（ＰＥＯ）鎖とを組み合わせた固体電解質の合成が盛んに試みられている。例えば，特開昭６２－２０９１６９号公報にはシロキサンとＰＥＯとを白金触媒によるヒドロシリル化反応や放射線（電子線等）照射により架橋させ、得られた架橋物にリチウムイオンを分散させて，固体電解質としたものが開示されている。また、特開昭６３－１７０８５７号公報にはこれらの固体電解質を組み込んだリチウム電池が開示されている。しかし、これらの方法では、２種以上の原料を相溶させるために有機溶剤を用いる必要があった。有機溶剤の使用は一部の製品には適用できないばかりか工程の煩雑化を招き，また作業環境の悪化，周辺材料の損傷、最終生成物への有機溶剤の残留等を起こす恐れがあった。また有機溶剤により原料が相溶できても、

有機溶剤が蒸発する過程などで相分離を起こす等により架橋反応の完結性が完全には保証されず、結局製品の品質の低下、再現性のなさ等に結び付くため実用化には問題があった。さらに、特開平２－２３０６６７号公報にはポリエチレンオキシド鎖をグラフトしたポリスチレンにリチウム塩を分散させた固体電解質を組み込んだリチウム電池が開示されている。この方法においては材料の均質性は向上するものの，以下の欠点があった。すなわち，特開昭６３－１７０８５７号公報，特開平２－２３０６６７号公報等で述べられているリチウム塩を分散させる形式の固体電解質においては、電気伝導によりリチウムイオンと同時に負イオンの移動が起こるものであった。負イオンの移動は多くの場合弊害となることが多い。例えば、充放電時に負イオンの移動により電解質内に分極が起こることにより電極／電解質界面の構造が経時的に変化し，金属イオンの移動に伴う定常電流が流れなくなる。負イオンは正イオンとの電荷補償のために存在せざるを得ないが、その移動度をなるべく低下させること，すなわち，正イオン単独伝導型固体電解質の作製が試みられている。例えば，日本化学会１９８８春期年会講演番号２ＸIIＣ０８には、オクタメチルシクロテトラシロキサンとベンゼンスルホン酸メチルエステルをプラズマ重合させた後、ＰＥＯを複合させ、さらにヨウ化リチウムで処理することによりスルホネートイオンが固定されたリチウムイオン単独伝導型固体電解質薄膜が開示されている。しかし、この場合、プラズマ重合は、反応が複雑なため意図する高分子の構造を得ることは困難であり、完全なリチウムイオン単独伝導型固体電解質にはならないという欠点があった。さらに、プラズマ重合のため、応用範囲に制約があるという欠点があった。このように、現在まで提案されたリチウム電池は，たとえ固体電解質を組み込んだ場合であっても、いずれも固体電解質自体の特性あるいは製造方法に欠点を有していたため，電池の特性および製造法が満足すべきものではなかった。

【0003】本発明者らはかかる問題点を解決すべく鋭意検討した結果，特定の高分子共重合体架橋物中にリチウムイオンを分散させてなる材料が，上記のような欠点がなくイオン伝導性に優れ，しかも組成を操作することにより正イオン単独伝導型固体電解質材料になり得，リチウム電池の電解質として組み込んだ場合、上記のような欠点を払拭できることを見出し本発明に到達した。本発明の目的は安定した電圧，電流を与える全固体リチウム電池を提供するにある。

【0004】

【課題の解決手段とその作用】かかる本発明は，金属リチウム、リチウム合金もしくはリチウム挿入型炭素を活物質とする負極と，正極とが電解質を介して構成されているリチウム電池において，前記電解質が、炭化水素基を介してケイ素原子に結合した式，$-COO^{-}Li^{+}$ で

示されるリチウムカルボキシレート基を含有するポリオルガノシロキサン鎖とポリオキシアルキレン鎖含有高分子化合物とから構成された高分子共重合体架橋物からなることを特徴とするリチウム電池に関する。

【0005】これについて説明するに、本発明でいうリチウム電池とは全固体である一次電池および充放電可能な二次電池双方を指す。一次あるいは二次を決定する要因としては主に正極活物質の種類である。本発明では、リチウム電池の高性能化の1つとして先に述べたリチウムイオン単独伝導性を目的としているため、リチウム電池の形式としては、一次、二次どちらにおいてもいわゆるロッキングチェア型の構成にする必要がある。すなわち、正負両極における電池反応を司どるのはリチウムイオンのみとするものである。従って正極においては、リチウムイオンが挿入（放電時）、脱離（二次電池における充電時）する形式である必要がある。電池の構造としては負極－固体電解質－正極のサンドイッチ構造を有するものであり、大きさ、厚さおよび形態は限定しないが、典型的には面積数cm^2、厚さ約1mm程度のペーパー型からコイン型、スパイラル方式のシリンダー型まで多様のものが可能である。負極は代表的にはリチウム金属箔を用いるが、負極活物質としてのリチウム金属が電極反応に有効な形態で存在している導電性シートであれば特に限定されない。例えば、カーボンシートにリチウムなどが保持されたもの、あるいはリチウム－アルミニウム合金などが挙げられる。正極の活物質としては、上記電池反応を起こし得るものであれば特に限定されないが、典型的には無機層状化合物を用いる。例えば、二酸化マンガン、酸化ヴァナジウム、二硫化チタン、酸化コバルト、酸化ニッケル、硫化モリブデンやこれらの複合体等を用いる。これらの化合物は通常、脆く、また導電性が低いために、有機樹脂を粘結材として用い板状にする工夫がされたり、導電性付与剤としてカーボン粒子等が添加される。また、特に二次電池を構築する場合は、充放電のサイクルによる層状構造の不変性あるいはリチウムイオンの吸脱着性等から一部リチウム原子を構造に取り込ませた層状化合物を用いると好適である。

【0006】次いで上記高分子共重合体架橋物について説明するに、この架橋物はメチレン基、エチレン基、プロピレン基、ブチレン基、ペンチレン基、ヘキセレン基、ヘプチレン基、オクチレン基等の炭素数1～8のアルキレン基；フェニレン基、ナフチレン基等の炭素数8～20のアリーレン基で例示されるような炭化水素基を介してケイ素原子に結合した、式、$-COO^{-}Li^{+}$で示される化学構造を有するリチウムカルボキシレート基含有ポリオルガノシロキサン鎖とポリオキシアルキレン鎖含有高分子化合物とから構成されたものであればよく、その高分子化合物の種類、形態、架橋密度等については特に限定されない。

【0007】本発明の固体電解質は前述のような負イオンを含む基（$-COO^{-}$）が炭化水素基を介してケイ素原子に結合されているため、負イオンの移動度は極端に低い。従って、この高分子共重合体架橋物中ではリチウムイオンが負イオンから解離し、リチウムイオンが移動することによりイオン導電性が発現する。高分子共重合体架橋物内に存在する負イオンの種類が$-COO^{-}$のみであれば、本固体電解質材料はリチウムイオン単独伝導体として働く。

【0008】かかる固体電解質の製造方法について好ましい方法は、以下の方法が推奨される。「(A)1分子中に少なくとも2個のカルボキシル基含有炭化水素基を有するポリオルガノシロキサン、(B)1分子中に少なくとも2個の水酸基を有するポリオキシアルキレン鎖含有高分子化合物、および(C)リチウム金属原子を含むアルカリ化合物からなる混合物を脱水縮合反応により硬化せしめることにより製造する方法。」

【0009】これについて説明するに、(A)成分のポリオルガノシロキサンは、高分子共重合体架橋物を形成するためには1分子中に2個以上のカルボキシル基含有炭化水素基を有することが必要であり、また、このカルボキシル基含有炭化水素基が結合したシロキサン単位とそれ以外のシロキサン単位の比率が0.01～100の範囲内にあるものが好ましい。本成分の分子構造は直鎖状、分岐状、環状、網状、三次元構造の何れでもよいが、高分子共重合体架橋物の形成の容易さからその半数以上は直鎖状もしくは分岐状であることが好ましい。また、その分子量は特に限定されないが、製造の容易さ、高分子共重合体架橋物としての適度の硬さを得るためには100～100万の範囲内にあることが好ましい。(A)成分のカルボキシル基含有炭化水素基としては、例えば、一般式$HOOC-R^{1}-$（式中、R^{1}はメチレン基、エチレン基、プロピレン基、ブチレン基、ペンチレン基、ヘキシレン基、ヘプチレン基、オクチレン基等の炭素数1～8のアルキレン基またはフェニレン基、ナフチレン基等の炭素数6～20のアリーレン基である。）で示される基が挙げられ、これらの中でもカルボキシアルキル基が好ましく、カルボキシプロピル基が特に好ましい。(A)成分中のカルボキシル基含有炭化水素基以外の有機基としては、例えば、メチル基、エチル基、プロピル基等のアルキル基；フェニル基、トリル基、キシリル基等のアリール基；ベンジル基、フェネチル基等のアラルキル基が例示される。また、ケイ素原子に結合した基としては、少量の水素原子、アルコキシ基が含まれてもよい。経済性および良好な高分子共重合体架橋物の形成性の観点からはケイ素原子に結合したオルガノ基の半数以上はメチル基であることが好ましい。かかるポリオルガノシロキサンとしては、例えば、分子鎖両末端がトリメチルシロキシ基で封鎖されたメチルカルボキシプロピルシロキサン・ジメチルシロキサン共重合体、分子鎖両末端がトリメチルシロキシ基で封鎖されたメチルカル

ポキシプロピルシロキサン・メチルフェニルシロキサン共重合体が挙げられる。かかるポリオルガノシロキサンの合成方法としては種々の方法が知られているが、その1つの方法としてはシアノ基を有するオルガノジクロロシランとシアノ基を有さないオルガノジクロロシランを共加水分解して得られる環状物と末端停止剤とを硫酸水溶液中で攪拌し、シアノ基がカルボキシル基に転化する反応と開環重合を起こさせる方法が挙げられる。

【0010】(B)成分の高分子化合物は上記(A)成分の架橋剤であり、架橋剤としての働きをするためには、1分子中に少なくとも2個の水酸基を含有することが必要である。また、高イオン伝導性発現のため高分子共重合体架橋物中にはポリオキシアルキレン鎖を有することが＊好ましいが、そのためには(B)成分の高分子化合物構造中にポリオキシアルキレン鎖を含有することが必要である。

【0011】ところで、(A)成分と(B)成分が互いに相溶することは工程中に溶剤を使用することが避けられるばかりか、架橋反応の完結、架橋生成物の構造、物性の良好な再現性をもたらすため大変重要なことである。(A)成分と相溶するための(B)成分の分子構造および化学構造についてはシロキサン単位を有していることが好ましく、高分子共重合体架橋物の形成の容易さ等から一般式

【化1】

$$R^2_3SiO\Big(\underset{R^2}{\overset{R^2}{Si}}O\Big)_a\Big(\underset{R^3-(R^4O)_p-H}{\overset{R^2}{Si}}O\Big)_b\Big(\underset{R^3-(R^4O)_p-R^5}{\overset{R^2}{Si}}O\Big)_cSiR^2_3$$

(式中、R^2は1価の有機基、R^3は2価の有機基、R^4はアルキレン基、R^5は1価の有機基、a、cは0～1000の整数、bは2～1000の整数、pは2～100の整数である。)で示される末端に水酸基を有するポリオキシアルキレン鎖を少なくとも2本グラフト鎖として有するポリオルガノシロキサンが好ましい。かかるオルガノポリシロキサンは上式中、R^2は、メチル基、エチル基、プロピル基等のアルキル基；フェニル基、トリル基、キシリル基等のアリール基；ベンジル基、フェネチル基等のアラルキル基が例示される。また、一部、少量の水素原子、アルコキシ基が含まれてもよい。経済性および良好な高分子共重合体架橋物の形成性の観点からはR^2の半数以上はメチル基であることが好ましい。R^3はメチレン基、エチレン基、プロピレン基、ブチレン基、ペンチレン基、ヘキシレン基、ヘプチレン基、オクチレン基等の炭素数1～8のアルキレン基またはフェニレン基、ナフチレン基等のアリーレン基等の2価の有機基である。R^4はメチレン基、エチレン基、プロピレン基、ブチレン基、ペンチレン基、ヘキシレン基、ヘプチレン基等のアルキレン基である。R^5はメチル基、エチル基、プロピル基等のアルキル基；アセチル基またはプロピオニル基等のアシル基である。a、cは0～1000の範囲内であり、bは2～1000の範囲内であり、それぞれ特に限定されないが、(A)成分と(B)成分が相溶するためにはaと(b＋c)の比率は(1：5)～(5：1)の範囲内が好ましい。

【0012】かかるグラフト共重合体の合成方法としては種々の方法が知られているが、その1つの方法としては側鎖の一部が水素原子で置き換わったポリオルガノシロキサンに、片末端に不飽和炭化水素基を有し他末端にアシロキシ基を有するポリオキシアルキレンと、片末端に不飽和炭化水素基を有し他末端にトリメチルシリル基を有するポリオキシアルキレンを所定の比率によりヒドロシリル化反応によりグラフトさせ、しかる後に過剰量のアルコールによりグラフト末端のトリメチルシリル基のみを水酸基に転化する方法が挙げられる。

【0013】(B)成分は上記のような1分子中に少なくとも2個の水酸基を有し、構造中にポリオキシアルキレン鎖を含む高分子化合物であるが、より高いイオン伝導性を要求される場合には、この高分子化合物は一般式HO－(R^6O)q－H(式中、R^6はアルキレン基、qは1～100の整数である。)で示される分子鎖両末端に水酸基を有するポリオキシアルキレンまたはHO－(R^7O)r－R^8(式中、R^7はアルキレン基、R^8は1価の有機基、rは1～100の整数である。)で示される分子鎖片末端に水酸基を有するポリオキシアルキレンであることが好ましい。かかるポリオキシアルキレンの上式のR^6、R^7はメチレン基、エチレン基、プロピレン基、ブチレン基、ペンチレン基、ヘキシレン基、ヘプチレン基等のアルキレン基である。R^8はメチル基、エチル基、プロピル基等のアルキル基；アセチル基またはプロピオニル基等のアシル基である。q、rは1～100の範囲内であり、5～20の範囲内が好ましい。かかる分子鎖両末端に水酸基を有するポリオキシアルキレンまたは分子鎖片末端に水酸基を有するポリオキシアルキレンは上記(A)成分と縮合反応し、高分子共重合体架橋物中にポリオキシアルキレンの架橋鎖またはグラフト鎖の含有量を増加する働きをする。本発明においては、かかる架橋鎖またはグラフト鎖が存在しなくても高分子化合物中のポリオキシアルキレン鎖によりポリオキシアルキレンの架橋鎖またはグラフト鎖を形成させることはできる。しかし、(A)成分と(B)成分が相溶する条件にお

いては高分子化合物中のポリオキシアルキレン鎖の導入量には限界があるため、分子鎖両末端に水酸基を有するポリオキシアルキレンまたは分子鎖片末端に水酸基を有するポリオキシアルキレンを(B)成分中に含有させる方が好ましい。また本発明においては、高分子共重合体架橋物中にポリオキシアルキレンのグラフト鎖が若干存在した方がイオン伝導性が向上する傾向にある。

【0014】(C)成分は、リチウム原子を含むアルカリ化合物であり、その種類は特に限定されないが、水酸化物、アルコラート、水素化物等が好ましく、特に水酸化物の形態、すなわち水酸化リチウム（LiOH）が使用されることが好ましい。かかる(C)成分は、(A)成分と(B)成分のエステル化反応の触媒作用をすると同時に、最終的には(A)成分中のカルボキシル基を脱水によりリチウムカルボキシレート化する役割をする。その結果、高分子共重合体架橋物としては、負イオン（カルボキシレートイオン）はシロキサンポリマー鎖に固定され、対イオンである正イオン（リチウムイオン）が分散された形態になる。また、その分散量は高分子共重合体架橋物中のオキシアルキレン基のモル数［RO］に対するリチウムイオンのモル数［Li^+］の比率比［Li^+］／［RO］が0.005～0.25とすることが好ましく、より好ましくは0.02～0.1である。これはこの比が0.25を越えると高分子共重合体架橋物の極性が上がり、セグメントの運動性が悪くなり、また0.005未満になるとキャリア数の低下から高いイオン伝導性が得難くなるからである。また、(A)成分中のカルボキシル基のモル数と、(B)成分中の水酸基のモル数と(C)成分中のアルカリ当量の合計の比率は（1：10）～（10：1）の範囲内であり、（1.0：1.2）～（1.2：1.0）の範囲内が好ましい。これは（A）～(C)成分はいずれの比率でもエステル化反応が起こり、固体化した高分子共重合体架橋物が得られるが、(B)成分中の水酸基のモル数と(C)成分中のアルカリ当量の合計と(A)成分中のカルボキシル基のモル数の比が大幅に異なると、固体電解質材料中に未反応のカルボキシル基または水酸基が残存した状態となる傾向にある。この状態での固体電解質を電池に組み込んだ場合には、電極材との反応等の弊害が起こることが予想されるので、好ましくない。また、上記のモル比が1になれば、正イオン種はリチウムイオンのみ、負イオン種は固定されたカルボキシレートイオンのみとなり、完全なリチウムイオン単独伝導型固体電解質となる。

【0015】この方法においては(A)成分～(C)成分からなる混合物を脱水縮合反応により硬化させ高分子共重合体架橋物を形成させるのであるが、この架橋物は主に(A)成分中のカルボキシル基と(B)成分の水酸基とのエステル化反応によって形成されるものである。その反応手段としてはカルボキシル基と水酸基との反応に用いられている従来公知の反応手段、例えば、アルカリ等のエステル化反応触媒を使用し、常温または加熱下に反応させる方法が利用できる。また、加熱はこのエステル化反応を促進すると同時にエステル化反応によって発生した副生物である水を除去するために有効な技術手段であり、その温度は通常150℃以下である。また、この架橋反応は無溶媒の条件で行うことができる。(A)成分と(B)成分は攪拌等の操作で容易に均一に混合できる。(C)成分はオキシアルキレン鎖に対して溶解性を持つので、(B)成分に予め溶解させておくか、(A)成分と(B)成分を混合させた後に添加してもよい。(C)成分のオキシアルキレン鎖への溶解は攪拌等の操作でも可能だが、溶解時間短縮のためには加熱あるいは超音波照射等の操作あるいはごく少量の水の添加が効果的である。また、溶解工程において有機溶剤の使用が許容できる場合には、有機溶剤中で(A)成分～(C)成分を混合、溶解させ、しかる後に溶剤を蒸発させてもよい。かかる有機溶剤は特に限定されないが、例えば、テトラヒドロフラン、ジオキサン、アセトニトリル、ジメチルホルムアミド、ジメチルスルホキシドが挙げられる。また、このエステル化反応は副生物として水を生成するので、最終的には(A)成分～(C)成分の混合体を減圧下に置くことが好ましく、例えば、常圧加熱下でエステル化反応をある程度進行させた後に減圧下で加熱し、生成した水の除去とエステル化反応の完結を同時に行う方法が推奨される。ただし、溶解工程に溶剤を使用した場合は、常圧下に有機溶剤の沸点以下でエステル化反応をある程度進行させた後に、有機溶剤を蒸発させ、しかる後に減圧下で加熱する必要がある。

【0016】本発明のリチウム電池は上記の正極、負極、固体電解質を組み合わせてなるものであるが、その構築法については特に限定しない。各々を別々に作製してから3者を組み合わせてもよい。しかし、一般的に界面における接触面積が大きいほど電池としての効率が高まることから、正極上に固体電解質原料の混合物をキャストし、架橋反応を行わせてフィルム化した後、負極を張り合わせる方法が推奨される。また、水分により、負極、固体電解質は変質を受けるため、電池の作製は乾燥空気、好ましくはアルゴン等の不活性ガスの雰囲気で行う必要がある。

【0017】

【実施例】以下、実施例にて本発明をより詳細に説明する。尚、固体電解質のイオン伝導率の測定は次の方法により行った。固体電解質をフィルム状に成型し、測定用試料とした。この試料の厚さをマイクロメーターで測定した後、試料の両面に直径1cmの円形プレート状の白金電極を密着し、この全体を任意の温度に設定できる減圧容器内に設置し、10^{-5}Torr以下の高真空まで減圧して試料の状態が十分に平衡に達した後、LCRメーター（横河ヒューレットパッカード社製4192A）により5Hz～13MHzの交流電圧を印加し、複素インピーダ

ンス法により伝導率を測定した。

【００１８】

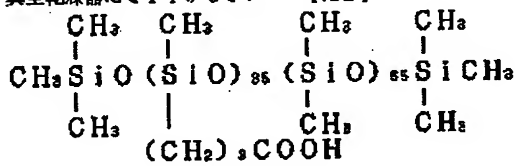
【実施例１】固体電解質として本発明によるもの（試料１）および特性比較のため．従来技術によるもの（試料２）を作製した。

【００１９】試料１

下記に示される化合物（１）０．３８４ｇ．化合物（２）０．４５０ｇ．化合物（３）０．１６７ｇ．水酸化リチウム１２．２mgおよび水０．１６ｇとを撹拌混合し、超音波を照射して十分に溶解させた。この溶液を３cm四方のテフロン製の皿に流し込み、ホットプレート上で１２０℃で２時間加熱した後．真空乾燥器にて１４０℃で＊４日間真空乾燥したところ．０．３mmの厚さの透明なフィルムを得た。このフィルムの赤外吸収スペクトルを調べたところ、水酸基および遊離カルボン酸に由来するピークが認められないこと．エステル生成によるカルボニル基の伸縮振動ピークが１７４０cm^{-1}にみられること、カルボキシレートイオンによる非対称伸縮振動ピークが１６００cm^{-1}にみられることから、エステル化反応はほぼ完全に行われていることがわかった。フィルムのイオン導電率を測定したところ．２５℃で２．０×１０$^{-7}$Ｓ・cm^{-1}の値が得られた。

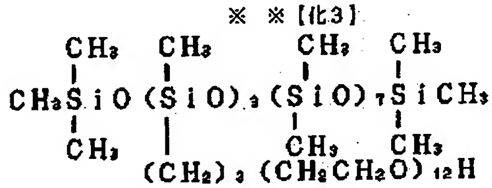
化合物（１）：

【化２】



化合物（２）：

※ ※【化３】



化合物（３）：HO（CH_2CH_2O）$_{12}$$CH_3$

【００２０】試料２

試料１で使用した化合物（１）０．２７８ｇ．化合物（２）０．５２７ｇ．化合物（３）０．１９５ｇおよび過塩素酸リチウム３０．８mgとを撹拌混合し．超音波を照射して十分に溶解せしめ．０．１規定塩酸エタノール溶液３μｌを加えた後、試料１と同様な加熱乾燥処理を行ったところ、０．３mmの厚さの透明なフィルムを得た。このフィルムの赤外吸収スペクトルを調べたところ、水酸基および遊離カルボン酸に由来するピークが認められないこと、エステル生成によるカルボニル基の伸縮振動ピークが１７４０cm^{-1}にみられることことから．エステル化反応はほぼ完全に行われていることがわかった。イオン導電率を測定したところ、２５℃で４．８×１０$^{-5}$Ｓ・cm^{-1}の値が得られた。

【００２１】直流電圧印加試験

厚さ０．３mmの試料１および試料２の両面に直径１cm．厚さ０．１４mmのリチウム箔を密着し、この全体を減圧容器内に設置し．２５℃にて１０$^{-5}$Ｔｏｒｒ以下の高真空まで減圧して試料の状態が十分に平衡に達した後、両リチウム箔に１Ｖの直流電圧を印加し．流れる電流の経時変化を観察した。試料１では初期の電流５．２μＡが約２日間持続し．このイオン導電性材料が正イオン単独伝導型イオン導電性材料であることが確かめられた。これに対し、試料２では初期の電流７９μＡが２日後には４．４μＡまで低下した。次いで試料１または２の固体電解質を用いてリチウム電池を構成した。正極材料として用いたリチウムーマンガン複合酸化物は、能間らによってSanyoTechnical Review,20,114(1989)に述べられた方法により調製した。水酸化リチウム０．１１８ｇと化学合成二酸化マンガン１ｇをよく混合した後、３７５℃で２０時間空気中で加熱し目的物を得た。電極に成型する際には、このリチウムーマンガン複合酸化物３０mgと導電剤としてのアセチレンブラック２０mg．結着剤としてテフロン５mgを加え加圧成型して得た。かかる正極を用いて作製した電池の断面図を図１に示した。試料１または２の組み込まれたリチウム電池について充放電サイクルテストを行った。定電流（３．７７あるいは３７．７μＡ／cm^{2}）で充電時の上限電圧を３．５Ｖ．放電時の下限電圧を２．５Ｖとして行った。図２に代表的なサイクルにおける電圧ー時間曲線を示した。本発明で得られた試料１を組み込んだ電池（ａ）では．充放電の繰り返しにともなう効率の低下はほとんど見られないばかりか．さらに上昇する傾向にある。従来技術で得られた試料２を組み込んだ電池（ｂ）（比較例１）では充放電の繰り返しによる効率の低下がみられた。図３にはサイクル毎の放電容量の推移を示した。サイクル毎の放電容量は．試料１を組み込んだ電池（ａ）ではあまり変動せず安定しているのに対し、試料２を組み込んだ電池（ｂ）（比較例１）では安定性に欠け、次第に放電容量も低下

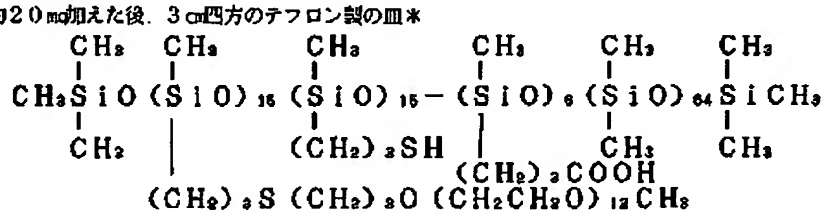
した。

【0022】

【実施例2】下記に示される化合物（4）10gを約500mlのトルエン／n－ブチルアルコール（1／1）混合溶媒に溶解させ、76.42mgの水酸化リチウムを加え．十分に攪拌し、化合物（4）中のカルボキシル基を完全にリチウムカルボキシレート化させた。しかる後に溶媒を完全に取り除き、得られた油状物0.772gと下記に示される化合物（5）0.154gおよび化合物（6）0.074gとを攪拌混合し、超音波を照射して十分に溶解させた。この混合物に光増感剤として（4－イソプロピル）フェニル-1-ハイドロキシイソプロピルケトンを約20mg加えた後．3cm四方のテフロン製の皿＊に流し込み、垂直上方より高圧水銀ランプからの160W／cmの紫外線を5cmの距離で6秒照射したところ、0.3mmの厚さの透明なフィルムを得た。さらにこれを70℃で2日間減圧乾燥させた後、イオン伝導率を測定したところ、25℃で1.6×10^{-7}S・cm^{-1}の値が得られた。また．実施例1と同様な直流電圧印加試験を行ったところ、4.7μAの電流が約2日間持続した。さらに実施例1と同様のリチウム電池を作製したところ、初期の放電容量は2.5mAh／gであり．20サイクル目には2.3mAh／gとなった。

化合物（4）：

【化4】



化合物（5）：

$CH_2=CH-CH_2O(CH_2CH_2O)_{12}CH_2-CH=CH_2$

化合物（6）：

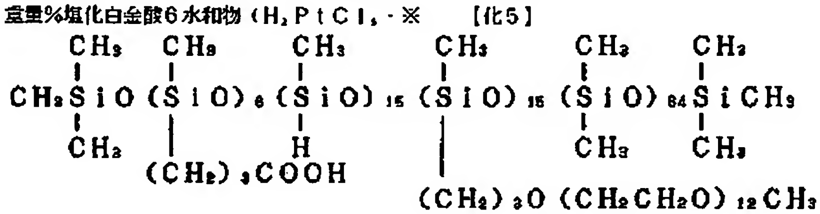
$CH_2=CH-CH_2O(CH_2CH_2O)_{12}CH_3$

【0023】

【実施例3】下記に示される化合物（7）10gを約500mlのトルエン／n－ブチルアルコール（1／1）混合溶媒に溶解させ、86.67mgの水酸化リチウムを加え．十分に攪拌し、化合物（7）中のカルボキシル基を完全にリチウムカルボキシレート化させた。しかる後に溶媒を完全に取り除き、得られた油状物0.749gと実施例1で使用した化合物（5）0.170gおよび化合物（6）0.081gとを攪拌混合し、超音波を照射して十分に溶解させた。この混合物にヒドロシリル化触媒として2重量%塩化白金酸6水和物（H_2PtCl_6・※$6H_2O$）イソプロピルアルコール溶液を2.47μl加えた後、3cm四方のテフロン製の皿に流し込み．70℃に調整されたオーブン内で2時間加熱したところ．0.3mmの厚さの透明なフィルムを得た。さらにこれを70℃で2日間減圧乾燥させた後、イオン伝導率を測定したところ、25℃で1.8×10^{-7}S・cm^{-1}の値が得られた。また、実施例1と同様な直流電圧印加試験を行ったところ、4.9μAの電流が約2日間持続した。さらに実施例1と同様のリチウム電池を作製したところ．初期の放電容量は3.5mAh／gであり、20サイクル目には2.9mAh／gとなった。

化合物（7）：

【化5】



【0024】

【発明の効果】本発明のリチウム電池は金属リチウム、リチウム合金もしくはリチウム挿入型炭素を活物質とする負極と、正極とが電解質を介して構成されているリチウム電池において、前記電解質が、炭化水素基を介してケイ素原子に結合した 式．$-COO^-Li^+$ で示されるリチウムカルボキシレート基を含有するポリオルガノシロキサン鎖とポリオキシアルキレン鎖とから構成された高分子共重合体架橋物からなるので．安定した電圧と電流を与え、高い信頼性を有するという特徴がある。

【図面の簡単な説明】

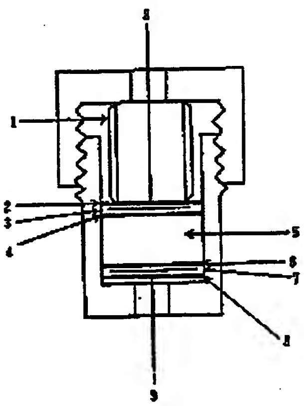
【図1】図1は本発明のリチウム電池の断面図である。

【図2】図2aは実施例1で得られたリチウム電池の定電流（3.77μA／cm²）下での充放電による電圧の時間的変化を示し．図2bは比較例1の定電流（37.7μA／cm²）下での充放電による電圧の時間変化を示したものである。尚、図2aおよび図2bにおいてvは電圧であり、tは経過時間である。

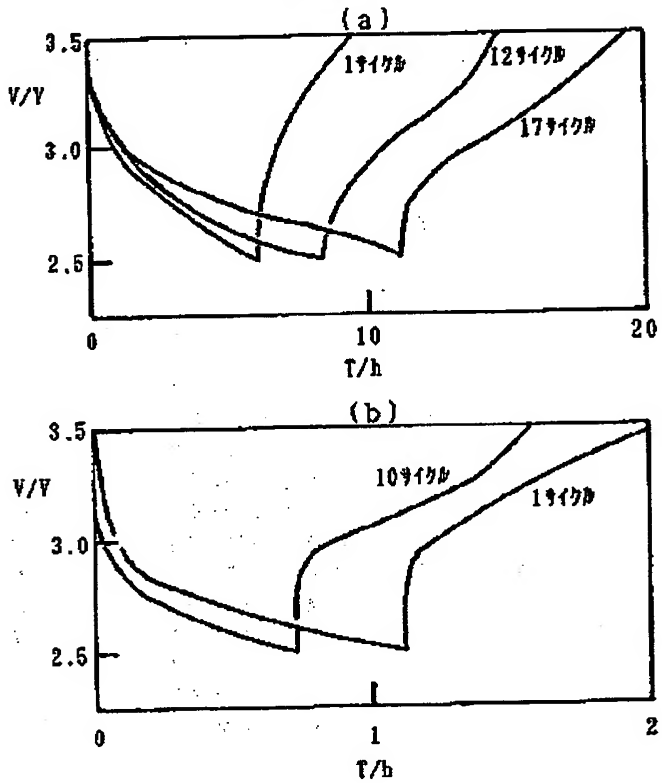
【図3】図3aは実施例1で得られたリチウム電池の定電流（3.77μA／cm²）下での充放電による放電容量

のサイクル毎の推移を示し、図3ｂは比較例1のリチウム電池の定電流（37.7μA／㎠）下での充放電による放電容量のサイクル毎の推移を示したものである。尚、図3ａおよび図3ｂにおいてＤ.Ｃ.は放電容量であり、Ｃ.Ｔ.はサイクル数である。1はテフロン製スペーサー、2はニッケル網、3はニッケル網、4は正極（リチウム－マンガン複合酸化物）、5は固体電解質、6は負極（リチウム箔）、7はニッケル網（リチウム箔を圧着したもの）、8はニッケル網、9はリード線

【図1】

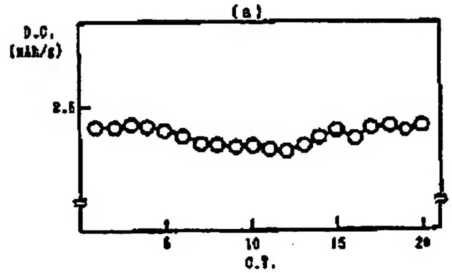


【図2】

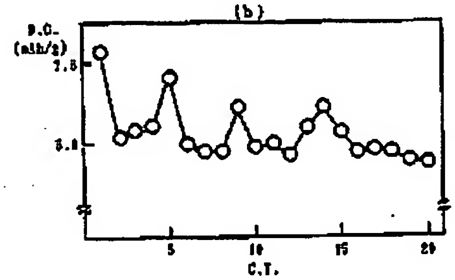


【図3】

(a)



(b)



CLAIMS

[Claim(s)]
[Claim 1] The formula, -COO-Li+ which the aforementioned electrolyte combined with the silicon atom through the hydrocarbon group in the lithium cell with which the negative electrode which makes an active material a metal lithium, a lithium alloy, or lithium insertion type carbon, and the positive electrode are constituted through the electrolyte Lithium cell characterized by the bird clapper from the macromolecule copolymer bridge formation object which consisted of a polyorganosiloxane chain containing the lithium carboxylate machine shown, and a polyoxyalkylene chain content high molecular compound.
[Claim 2] The lithium cell according to claim 1 manufactured by making the polyoxyalkylene chain content high molecular compound with which a macromolecule copolymer bridge formation object has at least two hydroxyl groups in the polyorganosiloxane which has at least two carboxyl group content hydrocarbon groups in (A)1 molecule, and (B)1 molecule, and the mixture which it becomes from the alkali compound containing (C) lithium metal atom harden by the dehydration condensation reaction.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to a lithium cell, the voltage stabilized by all solid-states in detail, and the lithium cell which gives current.

[0002]

[Description of the Prior Art] In recent years, as for the lithium cell, highly-efficient-izing, a miniaturization, and thin shape-ization are progressing much more with development of microelectronics. Improvement of the electrolyte with which the material of a negative electrode and a positive electrode and improvement of a gestalt are also included in it with last thing in this lithium cell is demanded, and a solid electrolyte is becoming important in the meaning which especially gives a solid state, high flexibility, and high fabricating-operation nature. Furthermore, various advanced properties, such as high ion conductivity, the high lithium ion transference number, high-reliability, and moisture resistance, are demanded. The solid electrolyte material which dissolved lithium salt in the macromolecule resin matrix, and it was made to distribute as such an electrolyte conventionally is known. Composition of the solid electrolyte which combined the polyorganosiloxane chain and the polyethylene-oxide (PEO) chain especially is tried briskly. For example, make a siloxane and PEO construct a bridge over JP,62-209169,A by the hydrosilylation reaction and radiation (electron ray etc.) irradiation by the platinum catalyst, the obtained bridge formation object is made to distribute a lithium ion, and what was made into the solid electrolyte is indicated. Moreover, the lithium cell incorporating these solid electrolytes is indicated by JP,63-170857,A. However, by these methods, in order to dissolve two or more sorts of raw materials, the organic solvent needed to be used. Use of the organic solvent had a possibility of having caused complicated-ization of about [being inapplicable to some products] or a process, and causing aggravation of a work environment, the injury on the charge of an edge strip, remains of the organic solvent to an end product, etc. Moreover, even if it could dissolve the raw material by the organic solvent, the conclusion nature of crosslinking reaction was not completely guaranteed by starting phase separation in process in which the organic solvent evaporates etc., but since it was connected with a lack [deterioration of the quality of a product, and repeatability] etc. after all, there was a problem in utilization. Furthermore, the lithium cell which included the solid electrolyte which made the polystyrene which carried out the graft of the polyethylene-oxide chain distribute lithium salt in JP,2-230667,A is indicated. Although the homogeneity of material improved in this method, there were the following faults. That is, in the solid electrolyte of form which distributes the lithium salt stated by JP,63-170857,A, JP,2-230667,A, etc., it was that to which movement of an anion takes place simultaneously with a lithium ion by electric conduction. In many cases, movement of an anion has many evils and bird clappers. For example, when polarization happens into an electrolyte by movement of an anion at the time of charge and discharge, the structure of an electrode / electrolyte interface will change with time, and the stationary current accompanying movement of a metal ion will not flow. Although an anion cannot but exist for charge compensation with a cation, production of reducing the mobility if possible, i.e., a cation independent conduction-type solid electrolyte, is tried. For example, after making Chemical Society of Japan 1988 spring annual convention lecture number 2XIIC08 carry out the plasma polymerization of the benzenesulfonic-acid methyl ester to octamethylcyclotetrasiloxane, it is made to compound PEO and the lithium ion independent conduction-type solid electrolyte thin

film to which sulfonate ion was fixed is indicated by processing with an iodation lithium further. However, the plasma polymerization had the fault of it having been difficult to acquire the structure of the macromolecule which a reaction means [complicated hatchet], and not becoming a perfect lithium ion independent conduction-type solid electrolyte, in this case. Furthermore, there was a fault that the application range had restrictions, for a plasma polymerization. Thus, even if it was the case where a solid electrolyte was incorporated even if, since the lithium cell proposed till present all had the fault in the property or the manufacture method of the solid electrolyte itself, it was not what the property and manufacturing method of a cell should satisfy.

[0003] When there were no above faults, the material which makes it come to distribute a lithium ion in a specific macromolecule copolymer bridge formation object was excellent in ion conductivity, and may have turned into cation independent conduction-type solid electrolyte material by moreover operating composition, as a result of inquiring wholeheartedly that this trouble should be solved, and it incorporated as an electrolyte of a lithium cell, this invention persons found out that the above faults could be wiped away, and reached this invention. The purpose of this invention is to offer all the solid-state lithium cells that give the stable voltage and current.

[0004]

[The solution means and operation of a technical problem] This this invention is the formula and -COO-Li+ which the aforementioned electrolyte combined with the silicon atom through the hydrocarbon group in the lithium cell with which the negative electrode which makes an active material a metal lithium, a lithium alloy, or lithium insertion type carbon, and the positive electrode are constituted through the electrolyte. It is related with the lithium cell characterized by the bird clapper from the macromolecule copolymer bridge formation object which consisted of a polyorganosiloxane chain containing the lithium carboxylate machine shown, and a polyoxyalkylene chain content high molecular compound.

[0005] The lithium cell as used in the field of this invention points out both the primary cell which are all solid-states, and the rechargeable battery in which charge and discharge are possible for explaining this. As a factor which determines primary or secondary, it is mainly the kind of positive active material. In this invention, since it aims at the lithium ion independent conductivity previously described as one of the highly-efficient-izing of a lithium cell, it is necessary to make second order so-called rocking-chair type composition also in which the first order as a form of a lithium cell. That is, managing the cell reaction in positive/negative two poles is taken only as a lithium ion. Therefore, it is necessary to be the form from which it sets to a positive electrode, and a lithium ion is inserted and (at the time of electric discharge) desorbed (at the time of the charge in a rechargeable battery). Although it does not have the sandwich structure of a negative-electrode-solid electrolyte-positive electrode as structure of a cell and a size, thickness, and a gestalt are not limited, Oshi's thing is typically possible even for a coin type and the cylinder type of a spiral method from area 2 and the paper type with a thickness of about about 1mm of several cm. Although a negative electrode uses a lithium metallic foil typically, especially if the lithium metal as a negative-electrode active material is the conductive sheet which exists with the gestalt effective in electrode reaction, it will not be limited. For example, the thing by which the lithium etc. was held, or a lithium-aluminium alloy is mentioned to a carbon sheet. Although it will not be limited as an active material of a positive electrode especially if the above-mentioned cell reaction can be started, an inorganic stratified compound is used typically. For example, manganese dioxide, oxidization vanadium, 2 titanium sulfides, cobalt oxide, nickel oxide, molybdenum sulfides, these complex, etc. are used. It is usually weak, and the work to which conductivity uses an organic resin for a low sake as caking additive, and it is made a tabular is carried out, or, as for these compounds, a carbon particle etc. is added as a conductive grant agent. Moreover, it is suitable if the stratified compound which made structure incorporate a lithium atom in part from the permanence of the layer structure by the cycle of charge and discharge or the absorptivity and desorptivity of a lithium ion is used when building especially a rechargeable battery.

[0006] subsequently, explaining the above-mentioned macromolecule copolymer bridge formation object this bridge formation object -- the alkylene machine of the carbon numbers 1-8, such as a methylene group, an ethylene, a propylene machine, a butylene machine, a pentylene machine, a

hexelene machine, a heptylene machine, and an octylene machine, -- a hydrocarbon group which is illustrated with the arylene machine of the carbon numbers 8-20, such as; phenylene group and a naphthylene machine That what is necessary is just to consist of the lithium carboxylate machine content polyorganosiloxane chains and polyoxyalkylene chain content high molecular compounds which were minded and were combined with the silicon atom and which have a formula and the chemical structure shown by -COO-Li+ It is not limited about the kind of the high molecular compound, a gestalt, and especially crosslinking density.
[0007] Since the basis (-COO-) in which the solid electrolyte of this invention contains the above anions is combined with the silicon atom through the hydrocarbon group, the mobility of an anion is extremely low. Therefore, in this macromolecule copolymer bridge formation object, a lithium ion dissociates from an anion, and when a lithium ion moves, ion conductivity is discovered. If the kind of anion which exists in a macromolecule copolymer bridge formation object is only -COO-, this solid electrolyte material will work as a lithium ion independent conductor.
[0008] The method of the following [method / desirable about the manufacture method of this solid electrolyte] is recommended. "How to manufacture by making the polyoxyalkylene chain content high molecular compound which has at least two hydroxyl groups in the polyorganosiloxane which has at least two carboxyl group content hydrocarbon groups in (A)1 molecule, and (B)1 molecule, and the mixture which consists of an alkali compound containing (C) lithium metal atom harden by the dehydration condensation reaction."
[0009] The ratio of the siloxane unit which it is required to have two or more carboxyl group content hydrocarbon groups, and this carboxyl group content hydrocarbon group combined in 1 molecule in order for the polyorganosiloxane of the (A) component to form a macromolecule copolymer bridge formation object for explaining this, and the other siloxane unit What is within the limits of 0.01-100 is desirable. Although any of the shape of a straight chain, the letter of branching, annular, reticulated, and the three-dimensional structure are sufficient as the molecular structure of this component, as for the ease of formation of a macromolecule copolymer bridge formation object to more than the half; it is desirable that they are the shape of a straight chain and a letter of branching. Moreover, although especially the molecular weight is not limited, in order to obtain the moderate hardness as the ease of manufacture, and a macromolecule copolymer bridge formation object, it is desirable that it is within the limits of 1 million-1 million. (A) As a carboxyl group content hydrocarbon group of a component, the basis shown by general formula HOOC-R1- (R1 is the arylene machine of the carbon numbers 6-20, such as an alkylene machine of the carbon numbers 1-8, such as a methylene group, an ethylene, a propylene machine, a butylene machine, a pentylene machine, a hexylene machine, a heptylene machine, and an octylene machine, or a phenylene group, and a naphthylene machine, among a formula.) is mentioned, for example, also in these, a carboxy (A) As organic machines other than the carboxyl group content hydrocarbon group in a component, aralkyl machines, such as aryl group; benzyls, such as alkyl group; phenyl groups, such as a methyl group, an ethyl group, and a propyl group, a tolyl group, and a xylyl group, and a phenethyl machine, are illustrated, for example. Moreover, as a basis combined with the silicon atom, a small amount of hydrogen atom and an alkoxy group may be contained. As for more than the half of the ORGANO machine combined with the silicon atom from a viewpoint of economical efficiency and the formation nature of a good macromolecule copolymer bridge formation object, it is desirable that it is a methyl group. As this polyorganosiloxane, the methyl carboxy propyl siloxane dimethylsiloxane copolymer by which chain both ends were blocked with the trimethylsiloxy machine, and the methyl carboxy propyl siloxane methylphenyl siloxane copolymer by which chain both ends were blocked with the trimethylsiloxy machine are mentioned, for example. Although various methods are learned as the synthetic method of this polyorganosiloxane, the annular object and end halt agent which are obtained by carrying out the cohydrolysis of the ORGANO dichlorosilane which has a cyano group as the one method, and the ORGANO dichlorosilane which does not have a cyano group are stirred in sulfuric-acid solution, and the reaction which a cyano group converts into a carboxyl group, and the method of making ring opening polymerization start are mentioned.
[0010] (B) The high molecular compound of a component is the cross linking agent of the above-mentioned (A) component, and in order to carry out the work as a cross linking agent, it needs to

contain at least two hydroxyl groups in 1 molecule. Moreover, although it is desirable to have polyoxyalkylene chain in a macromolecule copolymer bridge formation object for a high ion conductivity manifestation, for that, it is required in the high-molecular-compound structure of the (B) component to contain polyoxyalkylene chain.

[0011] By the way, it is very important that the (A) component and the (B) component dissolve mutually in order that using a solvent in process may bring about the conclusion of about [avoid] and crosslinking reaction, the structure of a bridge formation product, and the good repeatability of physical properties. (A) It is desirable to have the siloxane unit about the molecular structure and the chemical structure of the (B) component for dissolving with a component, and it is a general formula [-izing 1] from the ease of formation of a macromolecule copolymer bridge formation object etc.

$$R^2{}_3SiO(\underset{R^2}{\overset{R^2}{Si}}O)\,a\,(\underset{R^3-(R^4O)\,p-H}{\overset{R^2}{Si}}O)\,b\,(\underset{R^3-(R^4O)\,p-R^5}{\overset{R^2}{Si}}O)\,c\,SiR^2{}_3$$

(-- an organic machine univalent in R2, an organic machine divalent in R3, an organic machine univalent [4 / R] in an alkylene machine and R5, and a and c are / integer / of 2-1000 / and p of integer / of 0-1000 / and b / the integers of 2-100 among a formula The polyorganosiloxane which has polyoxyalkylene chain which has a hydroxyl group at the end shown by) as an at least 2 graft chain is desirable. As for this organopolysiloxane, aralkyl machines, such as aryl group; benzyls, such as alkyl group; phenyl groups, such as a methyl group, an ethyl group, and a propyl group, a tolyl group, and a xylyl group, and a phenethyl machine, are illustrated among an upper formula, as for R2. Moreover, a small amount of hydrogen atom and an alkoxy group may be contained in part. As for more than the half of R2, from a viewpoint of economical efficiency and the formation nature of a good macromolecule copolymer bridge formation object, it is desirable that it is a methyl group. R3 is divalent organic machines, such as arylene machines, such as an alkylene machine of the carbon numbers 1-8, such as a methylene group, an ethylene, a propylene machine, a butylene machine, a pentylene machine, a hexylene machine, a heptylene machine, and an octylene machine, or a phenylene group, and a naphthylene machine. R4 is alkylene machines, such as a methylene group, an ethylene, a propylene machine, a butylene machine, a pentylene machine, a hexylene machine, and a heptylene machine. R5 is acyl groups, such as an alkyl group; acetyl group or propionyl machines, such as a methyl group, an ethyl group, and a propyl group. Although a and c are within the limits of 0-1000, b is within the limits of 2-1000 and it is not limited especially, respectively, in order for the (A) component and the (B) component to dissolve, a and the ratio of (b+c) have desirable within the limits of - (1:5) (5:1).

[0012] Although various methods are learned as the synthetic method of this graft copolymer The polyoxyalkylene to which a part of side chain has an unsaturation hydrocarbon group at the piece end, and it has an acyloxy machine at the other ends as the one method at the polyorganosiloxane which replaced by the hydrogen atom, The graft of the polyoxyalkylene which has an unsaturation hydrocarbon group at the piece end, and has a trimethylsilyl machine at the other ends is carried out by the hydrosilylation reaction with a predetermined ratio. The method of converting only the trimethylsilyl machine of a graft end into a hydroxyl group by the alcohol of an excessive amount is mentioned to after an appropriate time.

[0013] (B) Although a component is a high molecular compound which has at least two hydroxyl groups in the above 1 molecules, and contains polyoxyalkylene chain in structure When higher ion conductivity is required, this high molecular compound is general formula HO-(R6O) q-H (an alkylene machine and q of R6 are the integers of 1-100 among a formula.). Polyoxyalkylene or HO-(R7O) r-R8 (an organic machine univalent [7 / R] in an alkylene machine and R8 and r are the integers of 1-100 among a formula.) which has a hydroxyl group in the chain both ends shown It is desirable that it is polyoxyalkylene which has a hydroxyl group at the piece end of a chain shown. R6 and R7 of the upper formula of this polyoxyalkylene are alkylene machines, such as a methylene group, an ethylene, a propylene machine, a butylene machine, a pentylene machine, a hexylene

machine, and a heptylene machine. R7 is acyl groups, such as an alkyl group; acetyl group or propionyl machines, such as a methyl group, an ethyl group, and a propyl group. q and r are within the limits of 1-100, and its within the limits of 5-20 is desirable. The condensation reaction of the polyoxyalkylene which has a hydroxyl group at the polyoxyalkylene or the piece end of a chain which has a hydroxyl group in these chain both ends is carried out to the above-mentioned (A) component, and it carries out the work which increases the content of the bridge formation chain of polyoxyalkylene, or a graft chain into a macromolecule copolymer bridge formation object. Even if this bridge formation chain or a graft chain does not exist, the bridge formation chain or graft chain of polyoxyalkylene can be made to form by the polyoxyalkylene chain in a high molecular compound in this invention. Since there is a limitation in the amount of introduction of the polyoxyalkylene chain in a high molecular compound in the conditions which the (A) component and the (B) component dissolve, make it however, more desirable to contain the polyoxyalkylene which has a hydroxyl group at the polyoxyalkylene or the piece end of a chain which has a hydroxyl group in chain both ends in the (B) component. Moreover, in this invention, the direction where the graft chain of polyoxyalkylene existed a little in the macromolecule copolymer bridge formation object is in the inclination whose ion conductivity improves.
[0014] (C) Although a component is an alkali compound containing a lithium atom and especially the kind is not limited, a hydroxide, an alcoholate, a hydride, etc. are desirable and it is desirable to be used, especially the gestalt of a hydroxide, i.e., a lithium hydroxide, (LiOH). This (C) component carries out the role which finally forms the carboxyl group in the (A) component into lithium carboxylate by dehydration at the same time it carries out the catalysis of the esterification reaction of the (A) component and the (B) component. Consequently, as a macromolecule copolymer bridge formation object, it is fixed to a siloxane polymer chain and an anion (carboxylate ion) becomes the gestalt by which the cation (lithium ion) which is a counter ion was distributed. Moreover, as for the variance, it is desirable that ratio ratio [of the number of mols [Li+] of a lithium ion to the number of mols of the oxy-alkylene machine in a macromolecule copolymer bridge formation object [RO]] [Li+]/[RO] sets to 0.005-0.25, and it is 0.02-0.1 more preferably. this -- this ratio if 0.25 is exceeded -- the polarity of a macromolecule copolymer bridge formation object -- going up -- the maneuverability of a segment -- bad -- becoming -- moreover -- It is because ion conductivity high from the fall of the number of carriers will become difficult to get if it becomes less than 0.005. Moreover, the number of mols of the carboxyl group in the (A) component, the number of mols of the hydroxyl group in the (B) component, and the ratio of the sum total of the alkali equivalent in the (C) component are within the limits of - (1:10) (10:1), and its within the limits of - (1.0:1.2) (1.2:1.0) is desirable. Although the macromolecule copolymer bridge-formation object which the esterification reaction occurred and solidified by any ratio is obtained, this has (A) - (C) component in the inclination which will be in the state where of an unreacted carboxyl group or an unreacted hydroxyl group remained in solid electrolyte material, when the ratios of the number of mols of the number of mols of the hydroxyl group in the (B) component, the sum total of the alkali equivalent in the (C) component, and the carboxyl group in the (A) component differ sharply. Since it is expected that evils, such as a reaction with electrode material, happen when the solid electrolyte in this state is included in a cell, it is not desirable. Moreover, if the above-mentioned mole ratio is set to 1, an anion kind will serve as only carboxylate ion to which only the lithium ion was fixed, and a cation kind will serve as a perfect lithium ion independent conduction-type solid electrolyte.
[0015] Although the mixture which consists of a (A) component - (C) component in this method is stiffened by the dehydration condensation reaction and a macromolecule copolymer bridge formation object is made to form, this bridge formation object is mainly formed of the esterification reaction of the carboxyl group in the (A) component, and the hydroxyl group of the (B) component. Esterification reaction catalysts, such as a conventionally well-known reaction means, for example, alkali etc., by which it is used for the reaction of a carboxyl group and a hydroxyl group as the reaction means, are used, and the method of making it react to the bottom of ordinary temperature or heating can be used. Moreover, in order that heating may remove the water which is the by-product generated by the esterification reaction at the same time it promotes this esterification reaction, it is an effective technical means, and the temperature is usually 150 degrees C or less. Moreover, this

crosslinking reaction can be performed on condition that a non-solvent. (A) A component and the (B) component are uniformly mixable easily by operation of stirring etc. (C) You may add, after making it dissolve in the (B) component beforehand or mixing the (A) component and the (B) component, since a component has solubility to an oxy-alkylene chain. (C) Although operation of stirring etc. is also possible for the dissolution to the oxy-alkylene chain of a component, for dissolution time shortening, operation of heating or ultrasonic irradiation or addition of very little water is effective. Moreover, when use of the organic solvent is permissible in a dissolution process, a (A) component - (C) component may be mixed and dissolved in the organic solvent, and a solvent may be evaporated after an appropriate time. Although especially this organic solvent is not limited, a tetrahydrofuran, a dioxane, an acetonitrile, a JIMECHI formamide, and dimethyl sulfoxide are mentioned, for example. Moreover, since this esterification reaction generates water as a by-product, it is desirable to put the mixture of a (A) component - (C) component under reduced pressure finally, for example, the method of heating under reduced pressure, after advancing an esterification reaction to some extent under ordinary-pressure heating, and performing simultaneously the removal of water and the conclusion of an esterification reaction which were generated is recommended. However, when a solvent is used for a dissolution process, after advancing an esterification reaction to some extent below with the boiling point of the organic solvent under an ordinary pressure, the organic solvent is evaporated and it is necessary to heat under reduced pressure after an appropriate time.

[0016] Although the lithium cell of this invention comes to combine the above-mentioned positive electrode, a negative electrode, and a solid electrolyte, it is not limited especially about the building method. You may combine three persons, after producing each separately. However, since the efficiency as a cell increases so that the touch area in an interface is generally large, after carrying out the cast of the mixture of a solid electrolyte raw material on a positive electrode, making crosslinking reaction perform and film-izing, the method of making a negative electrode rival is recommended. in order that [moreover,] a negative electrode and a solid electrolyte may receive transformation with moisture -- production of a cell -- dry air -- it is necessary to carry out in the atmosphere of inert gas, such as an argon, preferably

[0017]

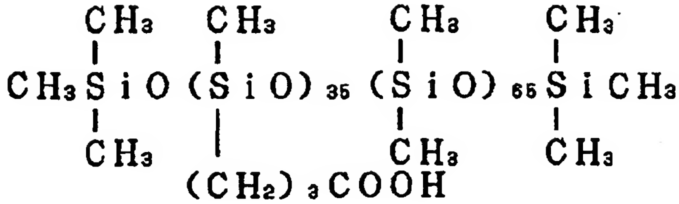
[Example] Hereafter, an example explains this invention to a detail more. In addition, measurement of the ionic conductivity of a solid electrolyte was performed by the following method. The solid electrolyte was cast in the shape of a film, and it considered as test sample. After measuring the thickness of this sample with a micrometer, the platinum electrode of the shape of a circular plate with a diameter of 1cm is stuck to both sides of a sample. After installing in the reduced pressure container which can set this whole as arbitrary temperature, decompressing to the high vacuum of 10 to 5 or less Torrs and the state of a sample fully reaching a balance, 5Hz - 13MHz alternating voltage was impressed by the LCR meter (4192made from YOKOGAWA ELECTRIC Hewlett Packard A), and conductivity was measured by the complex impedance method.

[0018]

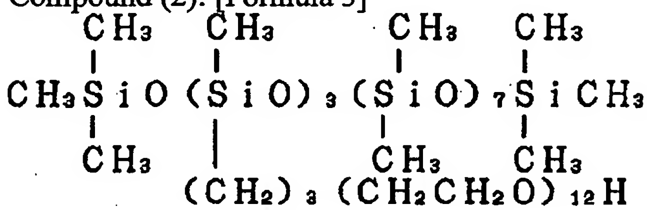
[Example 1] What is depended on the conventional technology (sample 2) was produced for the thing (sample 1) depended on this invention as a solid electrolyte, and property comparison.

[0019] Stirring mixture of compound (1)0.384g, compound (2)0.450g, compound (3)0.167g, 12.2mg of lithium hydroxides, and 0.16g of water shown in the sample 1 following was carried out, the ultrasonic wave was irradiated, and it was made to fully dissolve. After slushing this solution into the pan made from the Teflon of 3cm around and heating it at 120 degrees C on a hot plate for 2 hours, when the vacuum drying was carried out for four days at 140 degrees C by the vacuum dryer, the film with the transparent thickness of 0.3mm was obtained. Since that the peak originating in a hydroxyl group and an isolation carboxylic acid is not accepted, the stretching-vibration peak of the carbonyl group by esterification being seen by 1740cm-1, and the unsymmetrical stretching-vibration peak by carboxylate ion were seen by 1600cm-1 when the infrared absorption spectrum of this film was investigated, it turns out that the esterification reaction is performed nearly completely. When the ion conductivity of a film was measured, the value of 2.0x10-7 S-cm -1 was acquired at 25 degrees C.

Compound (1): [Formula 2]



Compound (2): [Formula 3]



Compound (3): HO(CH2CH2O)12CH3 [0020] After having carried out stirring mixture of compound (1)0.278g, compound (2)0.527g, compound (3)0.195g, and 30.8mg of lithium perchlorates used by sample 2 sample 1, having irradiated the ultrasonic wave, making it fully dissolve and adding 3micro of decinormal hydrochloric-acid ethanol solutions l, when the same stoving processing as a sample 1 was performed, the film with the transparent thickness of 0.3mm was obtained. When the infrared absorption spectrum of this film was investigated, it turns out [that the peak originating in a hydroxyl group and an isolation carboxylic acid is not accepted, and / as which the stretching-vibration peak of the carbonyl group by esterification is regarded by 1740cm-1] that the shell and the esterification reaction are rattlingly performed nearly completely. When ion conductivity was measured, the value of 4.8x10-5 S-cm -1 was acquired at 25 degrees C.

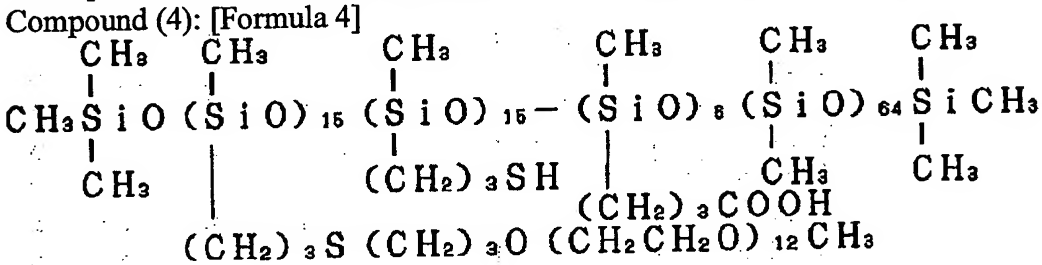
[0021] The lithium foil with a diameter [of 1cm] and a thickness of 0.14mm was stuck to both sides of the sample 1 with a direct-current-voltage impression examination thickness of 0.3mm and a sample 2, this whole was installed in the reduced pressure container, after it decompressed to the high vacuum of 10 to 5 or less Torrs at 25 degrees C and the state of a sample fully reached the balance, the direct current voltage of 1V was impressed to both the lithiums foil, and flowing aging of current was observed. By the sample 1, 5.2micro of early current A continued for about two days, and it was confirmed that this ion conductivity material is cation independent conduction-type ion conductivity material. On the other hand, two days after by the sample 2, 79micro of early current A fell to 4.4microA. Subsequently, the lithium cell was constituted using the solid electrolyte of samples 1 or 2. The lithium-manganese multiple oxide used as a positive-electrode material was prepared by the method stated to SanyoTechnical Review and 20,114 (1989) by Noma and others. Lithium hydroxide After often mixing 0.118g and 1g of chemosynthesis manganese dioxide, it heated in 20-hour air at 375 degrees C, and the specified substance was obtained. When casting to an electrode, Teflon 5mg was added as acetylene black 20mg as 30mg of this lithium-manganese multiple oxide, and an electric conduction agent, and a binder, pressurization molding was carried out, and it obtained. The cross section of the cell produced using this positive electrode was shown in drawing 1 . The charge-and-discharge cycle test was performed about the lithium cell with which samples 1 or 2 were incorporated. 3.5V and minimum voltage at the time of electric discharge were performed for the upper limit voltage at the time of charge as 2.5V by the constant current (3.77 or 37.7microA/cm -2). The voltage-time curve in a cycle typical to drawing 2 was shown. By the cell (a) incorporating the sample 1 obtained by this invention, not seeing and the inclination to go up further has most decline in the efficiency accompanying the repeat of charge and discharge. In the cell (b) incorporating the sample 2 obtained with the conventional technology, and the (example 1 of comparison), decline in the efficiency by the repeat of charge and discharge was seen. Transition of the service capacity for every cycle was shown in drawing 3 . To having seldom changed the service capacity for every cycle by the cell (a) incorporating the sample 1, but being stable, in the cell (b) incorporating the sample 2, and the (example 1 of comparison), stability was missing and service capacity also fell gradually.

[0022]

[Example 2] Compound (4)10g shown below was dissolved in about 500ml toluene / n-butyl alcohol (1/1) mixed solvent, the 76.42mg lithium hydroxide was added, it fully stirred, and the carboxyl

group in a compound (4) was made to form into lithium carboxylate completely. Stirring mixture of compound (5)0.154g which removes a solvent completely after an appropriate time, and is shown in 0.772g of obtained oily matter and the following, and the compound (6)0.074g was carried out, the ultrasonic wave was irradiated, and it was made to fully dissolve. After adding about 20mg of phenyl-1-hide ROKISHI isopropyl ketones to this mixture as a photosensitizer (4-isopropyl), when it slushed into the pan made from the Teflon of 3cm around and the ultraviolet rays of 160 W/cm from a high-pressure mercury lamp were irradiated for 6 seconds in 5cm distance from the perpendicular upper part, the film with the transparent thickness of 0.3mm was obtained. After carrying out reduced pressure drying of this for two days at 70 degrees C furthermore, when ionic conductivity was measured, the value of 1.6x10-7 S-cm -1 was acquired at 25 degrees C. Moreover, when the same direct-current-voltage impression examination as an example 1 was performed, the current of 4.7microA continued for about two days. When the still more nearly same lithium cell as an example 1 was produced, early service capacity is 2.5 mAh/g and became 20 cycle eye with 2.3 mAh/g.

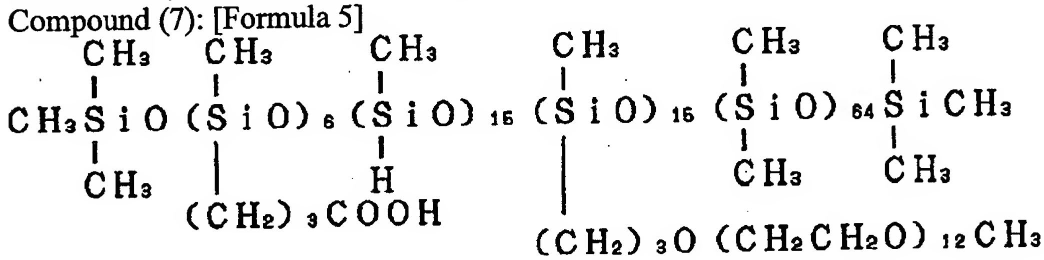
Compound (4): [Formula 4]



Compound (5): CH2=CH-CH2O(CH2CH2O)12CH2-CH=CH2 compound (6):CH2=CH-CH2O (CH2CH2O)12CH3 [0023]

[Example 3] Compound (7)10g shown below was dissolved in about 500ml toluene / n-butyl alcohol (1/1) mixed solvent, the 86.67mg lithium hydroxide was added, it fully stirred, and the carboxyl group in a compound (7) was made to form into lithium carboxylate completely. Stirring mixture of compound (5)0.170g which removed the solvent after an appropriate time completely, and used it for it in 0.749g of obtained oily matter and the example 1, and the compound (6)0.081g was carried out, the ultrasonic wave was irradiated, and it was made to fully dissolve. After 2.47microl Adding a chloroplatinic-acid 6 hydrate (H2PtCl6.6H2O) isopropyl alcohol solution to this mixture 2% of the weight as a hydrosilylation catalyst, it slushed into the pan made from the Teflon of 3cm around, and when heated within the oven adjusted to 70 degrees C for 2 hours, the film with the transparent thickness of 0.3mm was obtained. After carrying out reduced pressure drying of this for two days at 70 degrees C furthermore, when ionic conductivity was measured, the value of 1.8x10-7 S-cm -1 was acquired at 25 degrees C. Moreover, when the same direct-current-voltage impression examination as an example 1 was performed, the current of 4.9microA continued for about two days. When the still more nearly same lithium cell as an example 1 was produced, early service capacity is 3.5 mAh/g and became 20 cycle eye with 2.9 mAh/g.

Compound (7): [Formula 5]



[0024]

[Effect of the Invention] In the lithium cell with which the negative electrode to which the lithium cell of this invention makes an active material a metal lithium, a lithium alloy, or lithium insertion type carbon, and the positive electrode are constituted through the electrolyte The aforementioned electrolyte combined with the silicon atom through the hydrocarbon group. A formula, -COO-Li+ Since it consists of a macromolecule copolymer bridge formation object which consisted of a polyorganosiloxane chain containing the lithium carboxylate machine shown, and polyoxyalkylene

chain The stable voltage and stable current are given and there is the feature of having high reliability.

[Translation done.]

TECHNICAL FIELD

[Industrial Application] this invention relates to a lithium cell, the voltage stabilized by all solid-states in detail, and the lithium cell which gives current.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] In the lithium cell with which the negative electrode to which the lithium cell of this invention makes an active material a metal lithium, a lithium alloy, or lithium insertion type carbon, and the positive electrode are constituted through the electrolyte The aforementioned electrolyte combined with the silicon atom through the hydrocarbon group. A formula, -COO-Li+ Since it consists of a macromolecule copolymer bridge formation object which consisted of a polyorganosiloxane chain containing the lithium carboxylate machine shown, and polyoxyalkylene chain, the stable voltage and stable current are given and there is the feature of having high reliability.

[Translation done.]

TECHNICAL PROBLEM

[Description of the Prior Art] In recent years, as for the lithium cell, highly-efficient-izing, a miniaturization, and thin shape-ization are progressing much more with development of microelectronics. Improvement of the electrolyte with which the material of a negative electrode and a positive electrode and improvement of a form are also included in it with last thing in this lithium cell is demanded, and a solid electrolyte is becoming important in the meaning which especially gives a solid state, high flexibility, and high fabricating-operation nature. Furthermore, various advanced properties, such as high ion conductivity, the high lithium ion transference number, high-reliability, and moisture resistance, are demanded. The solid electrolyte material which dissolved lithium salt in the macromolecule resin matrix, and it was made to distribute as such an electrolyte conventionally is known. Composition of the solid electrolyte which combined the polyorganosiloxane chain and the polyethylene-oxide (PEO) chain especially is tried briskly. For example, make a siloxane and PEO construct a bridge over JP,62-209169,A by the hydrosilylation reaction and radiation (electron ray etc.) irradiation by the platinum catalyst, the obtained bridge formation object is made to distribute a lithium ion, and what was made into the solid electrolyte is indicated. Moreover, the lithium cell incorporating these solid electrolytes is indicated by JP,63-170857,A. However, by these methods, in order to dissolve two or more sorts of raw materials, the organic solvent needed to be used. Use of the organic solvent had a possibility of having caused complicated-ization of about [being inapplicable to some products] or a process, and causing aggravation of a work environment, the injury on the charge of an edge strip, remains of the organic solvent to an end product, etc. Moreover, even if it could dissolve the raw material by the organic solvent, the conclusion nature of crosslinking reaction was not completely guaranteed by starting phase separation in process in which the organic solvent evaporates etc., but since it was connected with a lack [deterioration of the quality of a product, and repeatability] etc. after all, there was a problem in utilization. Furthermore, the lithium cell which included the solid electrolyte which made the polystyrene which carried out the graft of the polyethylene-oxide chain distribute lithium salt in JP,2-230667,A is indicated. Although the homogeneity of material improved in this method, there were the following faults. That is, in the solid electrolyte of form which distributes the lithium salt stated by JP,63-170857,A, JP,2-230667,A, etc., it was that to which movement of an anion takes place simultaneously with a lithium ion by electric conduction. In many cases, movement of an anion has many evils and bird clappers. For example, when polarization happens into an electrolyte by movement of an anion at the time of charge and discharge, the structure of an electrode / electrolyte interface will change with time, and the stationary current accompanying movement of a metal ion will not flow. Although an anion cannot but exist for charge compensation with a cation, production of reducing the mobility if possible, i.e., a cation independent conduction-type solid electrolyte, is tried. For example, after making Chemical Society of Japan 1988 spring annual convention lecture number 2XIIC08 carry out the plasma polymerization of the benzenesulfonic-acid methyl ester to octamethylcyclotetrasiloxane, it is made to compound PEO and the lithium ion independent conduction-type solid electrolyte thin film to which sulfonate ion was fixed is indicated by processing with an iodation lithium further. However, the plasma polymerization had the fault of it having been difficult to acquire the structure of the macromolecule which a reaction means [complicated hatchet], and not becoming a perfect lithium ion independent conduction-type solid electrolyte, in this case. Furthermore, there was a fault that the application range had restrictions, for a plasma polymerization. Thus, even if it was the case

where a solid electrolyte was incorporated even if, since the lithium cell proposed till present all had the fault in the property or the manufacture method of the solid electrolyte itself, it was not what the property and manufacturing method of a cell should satisfy.

[0003] When there were no above faults, the material which makes it come to distribute a lithium ion in a specific macromolecule copolymer bridge formation object was excellent in ion conductivity, and may have turned into cation independent conduction-type solid electrolyte material by moreover operating composition, as a result of inquiring wholeheartedly that this trouble should be solved, and it incorporated as an electrolyte of a lithium cell, this invention persons found out that the above faults could be wiped away, and reached this invention. The purpose of this invention is to offer all the solid-state lithium cells that give the stable voltage and current.

[Translation done.]

OPERATION

[The solution means and operation of a technical problem] In the lithium cell with which the negative electrode to which this this invention makes an active material a metal lithium, a lithium alloy, or lithium insertion type carbon, and the positive electrode are constituted through the electrolyte The formula, -COO-Li+ which the aforementioned electrolyte combined with the silicon atom through the hydrocarbon group It is related with the lithium cell characterized by the bird clapper from the macromolecule copolymer bridge formation object which consisted of a polyorganosiloxane chain containing the lithium carboxylate machine shown, and a polyoxyalkylene chain content high molecular compound.

[0005] The lithium cell as used in the field of this invention points out both the primary cell which are all solid-states, and the rechargeable battery in which charge and discharge are possible for explaining this. As a factor which determines primary or secondary, it is mainly the kind of positive active material. In this invention, since it aims at the lithium ion independent conductivity previously described as one of the highly-efficient-izing of a lithium cell, it is necessary to make second order so-called rocking-chair type composition also in which the first order as a form of a lithium cell. That is, managing the cell reaction in positive/negative two poles is taken only as a lithium ion. Therefore, it is necessary to be the form from which it sets to a positive electrode, and a lithium ion is inserted and (at the time of electric discharge) desorbed (at the time of the charge in a rechargeable battery). Although it does not have the sandwich structure of a negative-electrode-solid electrolyte-positive electrode as structure of a cell and a size, thickness, and a gestalt are not limited, Oshi's thing is typically possible even for a coin type and the cylinder type of a spiral method from area 2 and the paper type with a thickness of about about 1mm of several cm. Although a negative electrode uses a lithium metallic foil typically, especially if the lithium metal as a negative-electrode active material is the conductive sheet which exists with the gestalt effective in electrode reaction, it will not be limited. For example, the thing by which the lithium etc. was held, or a lithium-aluminium alloy is mentioned to a carbon sheet. Although it will not be limited as an active material of a positive electrode especially if the above-mentioned cell reaction can be started, an inorganic stratified compound is used typically. For example, manganese dioxide, oxidization vanadium, 2 titanium sulfides, cobalt oxide, nickel oxide, molybdenum sulfides, these complex, etc. are used. It is usually weak, and the work to which conductivity uses an organic resin for a low sake as caking additive, and it is made a tabular is carried out, or, as for these compounds, a carbon particle etc. is added as a conductive grant agent. Moreover, it is suitable if the stratified compound which made structure incorporate a lithium atom in part from the permanence of the layer structure by the cycle of charge and discharge or the absorptivity and desorptivity of a lithium ion is used when building especially a rechargeable battery.

[0006] subsequently, explaining the above-mentioned macromolecule copolymer bridge formation object this bridge formation object -- the alkylene machine of the carbon numbers 1-8, such as a methylene group, an ethylene, a propylene machine, a butylene machine, a pentylene machine, a hexelene machine, a heptylene machine, and an octylene machine, -- a hydrocarbon group which is illustrated with the arylene machine of the carbon numbers 8-20, such as; phenylene group and a naphthylene machine It consisted of the lithium carboxylate machine content polyorganosiloxane chains and polyoxyalkylene chain content high molecular compounds which were minded and were combined with the silicon atom and which have a formula and the chemical structure shown by -

COO-Li+. About the kind of the high molecular compound, a gestalt, and especially crosslinking density, it is not limited that what is necessary is just to be.
[0007] Since the basis (-COO-) in which the solid electrolyte of this invention contains the above anions is combined with the silicon atom through the hydrocarbon group, the mobility of an anion is a low extremely. Therefore, in this macromolecule copolymer bridge formation object, a lithium ion dissociates from an anion, and when a lithium ion moves, ion conductivity is discovered. If the kind of anion which exists in a macromolecule copolymer bridge formation object is only -COO-, this solid electrolyte material will work as a lithium ion independent conductor.
[0008] The method of the following [method / desirable about the manufacture method of this solid electrolyte] is recommended. "How to manufacture by making the polyoxyalkylene chain content high molecular compound which has at least two hydroxyl groups in the polyorganosiloxane which has at least two carboxyl group content hydrocarbon groups in (A)1 molecule, and (B)1 molecule, and the mixture which consists of an alkali compound containing (C) lithium metal atom harden by the dehydration condensation reaction."
[0009] The ratio of the siloxane unit which it is required to have two or more carboxyl group content hydrocarbon groups, and this carboxyl group content hydrocarbon group combined in 1 molecule in order for the polyorganosiloxane of the (A) component to form a macromolecule copolymer bridge formation object for explaining this, and the other siloxane unit What is within the limits of 0.01-100 is desirable. Although any of the shape of a straight chain, the letter of branching, annular, reticulated, and the three-dimensional structure are sufficient as the molecular structure of this component, as for the ease of formation of a macromolecule copolymer bridge formation object to more than the half, it is desirable that they are the shape of a straight chain and a letter of branching. Moreover, although especially the molecular weight is not limited, in order to obtain the moderate hardness as the ease of manufacture, and a macromolecule copolymer bridge formation object, it is desirable that it is within the limits of 1 million-1 million. (A) As the carboxyl group content hydrocarbon group of a component For example, the basis shown by general formula HOOC-R1- (R1 is the arylene machine of the carbon numbers 6-20, such as an alkylene machine of the carbon numbers 1-8, such as a methylene group, an ethylene, a propylene machine, a butylene machine, a pentylene machine, a hexylene machine, a heptylene machine, and an octylene machine, or a phenylene group, and a naphthylene machine, among a formula.) is mentioned, also in these, a carboxy alkyl group is desirable and especially a carboxy propyl group is desirable (A) As organic machines other than the carboxyl group content hydrocarbon group in a component, aralkyl machines, such as aryl group; benzyls, such as alkyl group; phenyl groups, such as a methyl group, an ethyl group, and a propyl group, a tolyl group, and a xylyl group, and a phenethyl machine, are illustrated, for example. Moreover, as a basis combined with the silicon atom, a small amount of hydrogen atom and an alkoxy group may be contained. As for more than the half of the ORGANO machine combined with the silicon atom from a viewpoint of economical efficiency and the formation nature of a good macromolecule copolymer bridge formation object, it is desirable that it is a methyl group. As this polyorganosiloxane, the methyl carboxy propyl siloxane dimethylsiloxane copolymer by which chain both ends were blocked with the trimethylsiloxy machine, and the methyl carboxy propyl siloxane methylphenyl siloxane copolymer by which chain both ends were blocked with the trimethylsiloxy machine are mentioned, for example. Although various methods are learned as the synthetic method of this polyorganosiloxane, the annular object and end halt agent which are obtained by carrying out the cohydrolysis of the ORGANO dichlorosilane which has a cyano group as the one method, and the ORGANO dichlorosilane which does not have a cyano group are stirred in sulfuric-acid solution, and the reaction which a cyano group converts into a carboxyl group, and the method of making ring opening polymerization start are mentioned.
[0010] (B) The high molecular compound of a component is the cross linking agent of the above-mentioned (A) component, and in order to carry out the work as a cross linking agent, it needs to contain at least two hydroxyl groups in 1 molecule. Moreover, although it is desirable to have polyoxyalkylene chain in a macromolecule copolymer bridge formation object for a high ion conductivity manifestation, for that, it is required in the high-molecular-compound structure of the (B) component to contain polyoxyalkylene chain.

[0011] By the way, it is very important that the (A) component and the (B) component dissolve mutually in order that using a solvent in process may bring about the conclusion of about [avoid] and crosslinking reaction, the structure of a bridge formation product, and the good repeatability of physical properties. (A) It is desirable to have the siloxane unit about the molecular structure and the chemical structure of the (B) component for dissolving with a component, and it is a general formula from the ease of formation of a macromolecule copolymer bridge formation object etc. [Formula 1]

$$R^2_3SiO\left(\underset{R^2}{\overset{R^2}{Si}}O\right)_a\left(\underset{R^3-(R^4O)_p-H}{\overset{R^2}{Si}}O\right)_b\left(\underset{R^3-(R^4O)_p-R^5}{\overset{R^2}{Si}}O\right)_cSiR^2_3$$

(-- an organic machine univalent in R2, an organic machine divalent in R3, an organic machine univalent [4 / R] in an alkylene machine and R5, and a and c are / integer / of 2-1000 / and p of integer / of 0-1000 / and b / the integers of 2-100 among a formula The polyorganosiloxane which has polyoxyalkylene chain which has a hydroxyl group at the end shown by) as an at least 2 graft chain is desirable. As for this organopolysiloxane, aralkyl machines, such as aryl group; benzyls, such as alkyl group; phenyl groups, such as a methyl group, an ethyl group, and a propyl group, a tolyl group, and a xylyl group, and a phenethyl machine, are illustrated among an upper formula, as for R2. Moreover, a small amount of hydrogen atom and an alkoxy group may be contained in part. As for more than the moiety of R2, from a viewpoint of economical efficiency and the plasticity of a good macromolecule copolymer bridge formation object, it is desirable that it is a methyl group. R3 is divalent organic machines, such as arylene machines, such as an alkylene machine of the carbon numbers 1-8, such as a methylene group, an ethylene, a propylene machine, a butylene machine, a pentylene machine, a hexylene machine, a heptylene machine, and an octylene machine, or a phenylene group, and a naphthylene machine. R4 is alkylene machines, such as a methylene group, an ethylene, a propylene machine, a butylene machine, a pentylene machine, a hexylene machine, and a heptylene machine. R5 is acyl groups, such as an alkyl group; acetyl group or propionyl machines, such as a methyl group, an ethyl group, and a propyl group. Although a and c are within the limits of 0-1000, b is within the limits of 2-1000 and it is not limited especially, respectively, in order for the (A) component and the (B) component to dissolve, a and the ratio of (b+c) have desirable within the limits of - (1:5) (5:1).

[0012] Although various methods are learned as the synthetic method of this graft copolymer The method of making carry out the graft of the polyoxyalkylene which has an unsaturation hydrocarbon group at the polyoxyalkylene which has an unsaturation hydrocarbon group at the piece end at the polyorganosiloxane which a part of side chain replaced by the hydrogen atom as the one method, and has an acyloxy machine at the other ends, and the piece end, and has a trimethylsilyl machine at the other ends by the hydrosilylation reaction with a predetermined ratio, and converting only the trimethylsilyl machine of a graft end into a hydroxyl group by the alcohol of an excessive amount after an appropriate time is mentioned.

[0013] (B) Although a component is a high molecular compound which has at least two hydroxyl groups in the above 1 molecules, and contains polyoxyalkylene chain in structure When higher ion conductivity is required This high molecular compound is general formula HO-(R6O) q-H (an alkylene machine and q of R6 are the integers of 1-100 among a formula.). Polyoxyalkylene or HO-(R7O) r-R8 (an organic machine univalent [7 / R] in an alkylene machine and R8 and r are the integers of 1-100 among a formula.) which has a hydroxyl group in the chain both ends shown It is desirable that it is polyoxyalkylene which has a hydroxyl group at the piece end of a chain shown. R6 and R7 of the upper formula of this polyoxyalkylene are alkylene machines, such as a methylene group, an ethylene, a propylene machine, a butylene machine, a pentylene machine, a hexylene machine, and a heptylene machine. R7 is acyl groups, such as an alkyl group; acetyl group or propionyl machines, such as a methyl group, an ethyl group, and a propyl group. q and r are within the limits of 1-100, and its within the limits of 5-20 is desirable. The condensation reaction of the polyoxyalkylene which has a hydroxyl group at the polyoxyalkylene or the piece end of a chain which has a hydroxyl group in these chain both ends is carried out to the above-mentioned (A) component,

and it carries out the work which increases the content of the bridge formation chain of polyoxyalkylene, or a graft chain into a macromolecule copolymer bridge formation object. Even if this bridge formation chain or a graft chain does not exist, the bridge formation chain or graft chain of polyoxyalkylene can be made to form by the polyoxyalkylene chain in a high molecular compound in this invention. Since there is a limitation in the amount of introduction of the polyoxyalkylene chain in a high molecular compound in the conditions which the (A) component and the (B) component dissolve, make it however, more desirable to contain the polyoxyalkylene which has a hydroxyl group at the polyoxyalkylene or the piece end of a chain which has a hydroxyl group in chain both ends in the (B) component. Moreover, in this invention, the direction where the graft chain of polyoxyalkylene existed a little in the macromolecule copolymer bridge formation object is in the inclination whose ion conductivity improves.

[0014] (C) Although a component is an alkali compound containing a lithium atom and especially the kind is not limited, a hydroxide, an alcoholate, a hydride, etc. are desirable and it is desirable to be used, especially the gestalt of a hydroxide, i.e., a lithium hydroxide, (LiOH). This (C) component carries out the role which finally forms the carboxyl group in the (A) component into lithium carboxylate by dehydration at the same time it carries out the catalysis of the esterification reaction of the (A) component and the (B) component. Consequently, as a macromolecule copolymer bridge formation object, it is fixed to a siloxane polymer chain and an anion (carboxylate ion) becomes the gestalt by which the cation (lithium ion) which is a counter ion was distributed. Moreover, as for the variance, it is desirable that ratio ratio [of the number of mols [Li+] of a lithium ion to the number of mols of the oxy-alkylene machine in a macromolecule copolymer bridge formation object [RO]] [Li+]/[RO] sets to 0.005-0.25, and it is 0.02-0.1 more preferably. this -- this ratio if 0.25 is exceeded -- the polarity of a macromolecule copolymer bridge formation object -- going up -- the maneuverability of a segment -- bad -- becoming -- moreover -- It is because ion conductivity high from the fall of the number of carriers will become difficult to get if it becomes less than 0.005. Moreover, the number of mols of the carboxyl group in the (A) component, the number of mols of the hydroxyl group in the (B) component, and the ratio of the sum total of the alkali equivalent in the (C) component are within the limits of - (1:10) (10:1), and its within the limits of - (1.0:1.2) (1.2:1.0) is desirable. Although the macromolecule copolymer bridge formation object with which the esterification reaction occurred and solidified (A) - (C) component by any ratio for this is obtained (B) When the ratios of the number of mols of the number of mols of the hydroxyl group in a component, the sum total of the alkali equivalent in the (C) component, and the carboxyl group in the (A) component differ sharply, be in the inclination which will be in the state where an unreacted carboxyl group or an unreacted hydroxyl group remained in solid electrolyte material. Since it is expected that evils, such as a reaction with electrode material, happen when the solid electrolyte in this state is included in a cell, it is not desirable. Moreover, if the above-mentioned mole ratio is set to 1, an anion kind will serve as only carboxylate ion to which only the lithium ion was fixed, and a cation kind will serve as a perfect lithium ion independent conduction-type solid electrolyte.

[0015] Although the mixture which consists of a (A) component - (C) component in this method is stiffened by the dehydration condensation reaction and a macromolecule copolymer bridge formation object is made to form, this bridge formation object is mainly formed of the esterification reaction of the carboxyl group in the (A) component, and the hydroxyl group of the (B) component. Esterification reaction catalysts, such as a conventionally well-known reaction means, for example, alkali etc., by which it is used for the reaction of a carboxyl group and a hydroxyl group as the reaction means, are used, and the method of making it react to the bottom of ordinary temperature or heating can be used. Moreover, in order that heating may remove the water which is the by-product generated by the esterification reaction at the same time it promotes this esterification reaction, it is an effective technical means, and the temperature is usually 150 degrees C or less. Moreover, this crosslinking reaction can be performed on condition that a non-solvent. (A) A component and the (B) component are uniformly mixable easily by operation of stirring etc. (C) You may add, after making it dissolve in the (B) component beforehand or mixing the (A) component and the (B) component, since a component has solubility to an oxy-alkylene chain. (C) Although operation of stirring etc. is also possible for the dissolution to the oxy-alkylene chain of a component, for dissolution time

shortening, operation of heating or ultrasonic irradiation or addition of very little water is effective. Moreover, when use of the organic solvent is permissible in a dissolution process, a (A) component - (C) component may be mixed and dissolved in the organic solvent, and a solvent may be evaporated after an appropriate time. Although especially this organic solvent is not limited, a tetrahydrofuran, a dioxane, an acetonitrile, a JIMECHI formamide, and dimethyl sulfoxide are mentioned, for example. Moreover, since this esterification reaction generates water as a by-product, it is desirable to put the mixture of a (A) component - (C) component under reduced pressure finally, for example, the method of heating under reduced pressure, after advancing an esterification reaction to some extent under ordinary-pressure heating, and performing simultaneously the removal of water and the conclusion of an esterification reaction which were generated is recommended. However, when a solvent is used for a dissolution process, after advancing an esterification reaction to some extent below with the boiling point of the organic solvent under an ordinary pressure, the organic solvent is evaporated and it is necessary to heat under reduced pressure after an appropriate time.

[0016] Although the lithium cell of this invention comes to combine the above-mentioned positive electrode, a negative electrode, and a solid electrolyte, it is not limited especially about the building method. You may combine three persons, after producing each separately. However, since the efficiency as a cell increases so that the touch area in an interface is generally large, after carrying out the cast of the mixture of a solid electrolyte raw material on a positive electrode, making crosslinking reaction perform and film-izing, the method of making a negative electrode rival is recommended. in order that [moreover,] a negative electrode and a solid electrolyte may receive transformation with moisture -- production of a cell -- dry air -- it is necessary to carry out in the atmosphere of inert gas, such as an argon, preferably.

[Translation done.]

EXAMPLE

[Example] Hereafter, an example explains this invention to a detail more. In addition, measurement of the ionic conductivity of a solid electrolyte was performed by the following method. The solid electrolyte was cast in the shape of a film, and it considered as test sample. After measuring the thickness of this sample with a micrometer, the platinum electrode of the shape of a circular plate with a diameter of 1cm is stuck to both sides of a sample. After installing in the reduced pressure container which can set this whole as arbitrary temperature, decompressing to the high vacuum of 10 to 5 or less Torrs and the state of a sample fully reaching a balance, 5Hz - 13MHz alternating voltage was impressed by the LCR meter (4192made from YOKOGAWA ELECTRIC Hewlett Packard A), and conductivity was measured by the complex impedance method.
[0018]
[Example 1] What is depended on the conventional technology (sample 2) was produced for the thing (sample 1) depended on this invention as a solid electrolyte, and property comparison.
[0019] Stirring mixture of compound (1)0.384g, compound (2)0.450g, compound (3)0.167g, 12.2mg of lithium hydroxides, and 0.16g of water shown in the sample 1 following was carried out, the ultrasonic wave was irradiated, and it was made to fully dissolve. After slushing this solution into the pan made from the Teflon of 3cm around and heating it at 120 degrees C on a hot plate for 2 hours, when the vacuum drying was carried out for four days at 140 degrees C by the vacuum dryer, the film with the transparent thickness of 0.3mm was obtained. Since that the peak originating in a hydroxyl group and an isolation carboxylic acid is not accepted, the stretching-vibration peak of the carbonyl group by esterification being seen by 1740cm-1, and the unsymmetrical stretching-vibration peak by carboxylate ion were seen by 1600cm-1 when the infrared absorption spectrum of this film was investigated, it turns out that the esterification reaction is performed nearly completely. When the ion conductivity of a film was measured, the value of 2.0x10-7 S-cm -1 was acquired at 25 degrees C.
Compound (1): [Formula 2]

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    CH3   CH3          CH3      CH3
    |     |            |        |
CH3SiO (SiO)35     (SiO)65  SiCH3
    |     |            |        |
    CH3   |            CH3      CH3
       (CH2)3COOH
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Compound (2): [Formula 3]

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    CH3   CH3        CH3   CH3
    |     |          |     |
CH3SiO (SiO)3    (SiO)7 SiCH3
    |     |          |     |
    CH3   |          CH3   CH3
       (CH2)3 (CH2CH2O)12H
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Compound (3): HO(CH2CH2O)12CH3 [0020] After having carried out stirring mixture of compound (1)0.278g, compound (2)0.527g, compound (3)0.195g, and 30.8mg of lithium perchlorates used by sample 2 sample 1, having irradiated the ultrasonic wave, making it fully dissolve and adding 3micro of decinormal hydrochloric-acid ethanol solutions l, when the same stoving processing as a sample 1

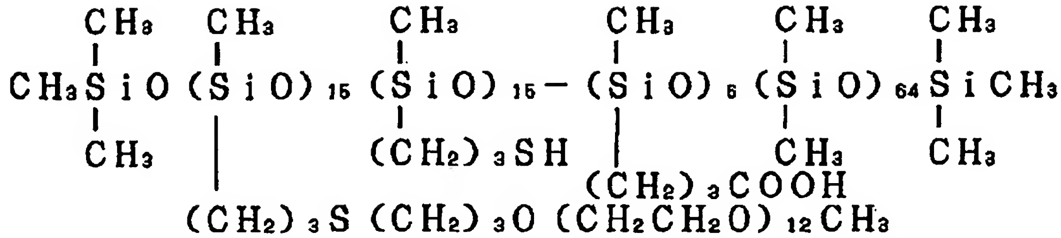
was performed, the film with the transparent thickness of 0.3mm was obtained. When the infrared absorption spectrum of this film was investigated, it turns out [that the peak originating in a hydroxyl group and an isolation carboxylic acid is not accepted, and / as which the stretching-vibration peak of the carbonyl group by esterification is regarded by 1740cm-1] that the shell and the esterification reaction are rattlingly performed nearly completely. When ion conductivity was measured, the value of 4.8x10-5 S-cm -1 was acquired at 25 degrees C.

[0021] The lithium foil with a diameter [of 1cm] and a thickness of 0.14mm was stuck to both sides of the sample 1 with a direct-current-voltage impression examination thickness of 0.3mm and a sample 2, this whole was installed in the reduced pressure container, after it decompressed to the high vacuum of 10 to 5 or less Torrs at 25 degrees C and the state of a sample fully reached the balance, the direct current voltage of 1V was impressed to both the lithiums foil, and flowing aging of current was observed. By the sample 1, 5.2micro of early current A continued for about two days, and it was confirmed that this ion conductivity material is cation independent conduction-type ion conductivity material. On the other hand, two days after by the sample 2, 79micro of early current A fell to 4.4microA. Subsequently, the lithium cell was constituted using the solid electrolyte of samples 1 or 2. The lithium-manganese multiple oxide used as a positive-electrode material was prepared by the method stated to SanyoTechnical Review and 20,114 (1989) by Noma and others. Lithium hydroxide After often mixing 0.118g and 1g of chemosynthesis manganese dioxide, it heated in 20-hour air at 375 degrees C, and the specified substance was obtained. When casting to an electrode, Teflon 5mg was added as acetylene black 20mg as 30mg of this lithium-manganese multiple oxide, and an electric conduction agent, and a binder, pressurization molding was carried out, and it obtained. The cross section of the cell produced using this positive electrode was shown in drawing 1 . The charge-and-discharge cycle test was performed about the lithium cell with which samples 1 or 2 were incorporated. 3.5V and minimum voltage at the time of electric discharge were performed for the upper limit voltage at the time of charge as 2.5V by the constant current (3.77 or 37.7microA/cm -2). The voltage-time curve in a cycle typical to drawing 2 was shown. By the cell (a) incorporating the sample 1 obtained by this invention, not seeing and the inclination to go up further has most decline in the efficiency accompanying the repeat of charge and discharge. In the cell (b) incorporating the sample 2 obtained with the conventional technology, and the (example 1 of comparison), decline in the efficiency by the repeat of charge and discharge was seen. Transition of the service capacity for every cycle was shown in drawing 3 . To having seldom changed the service capacity for every cycle by the cell (a) incorporating the sample 1, but being stable, in the cell (b) incorporating the sample 2, and the (example 1 of comparison), stability was missing and service capacity also fell gradually.

[0022]

[Example 2] Compound (4)10g shown below was dissolved in about 500ml toluene / n-butyl alcohol (1/1) mixed solvent, the 76.42mg lithium hydroxide was added, it fully stirred, and the carboxyl group in a compound (4) was made to form into lithium carboxylate completely. Stirring mixture of compound (5)0.154g which removes a solvent completely after an appropriate time, and is shown in 0.772g of obtained oily matter and the following, and the compound (6)0.074g was carried out, the ultrasonic wave was irradiated, and it was made to fully dissolve. After adding about 20mg of phenyl-1-hide ROKISHI isopropyl ketones to this mixture as a photosensitizer (4-isopropyl), when it slushed into the pan made from the Teflon of 3cm around and the ultraviolet rays of 160 W/cm from a high-pressure mercury lamp were irradiated for 6 seconds in 5cm distance from the perpendicular upper part, the film with the transparent thickness of 0.3mm was obtained. After carrying out reduced pressure drying of this for two days at 70 degrees C furthermore, when ionic conductivity was measured, the value of 1.6x10-7 S-cm -1 was acquired at 25 degrees C. Moreover, when the same direct-current-voltage impression examination as an example 1 was performed, the current of 4.7microA continued for about two days. When the still more nearly same lithium cell as an example 1 was produced, early service capacity is 2.5 mAh/g and became 20 cycle eye with 2.3 mAh/g.

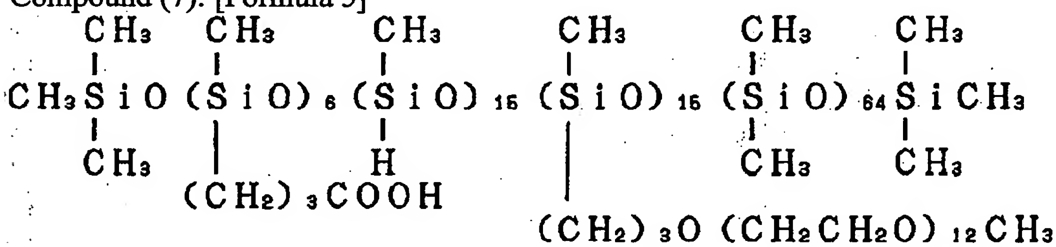
Compound (4): [Formula 4]



Compound (5): CH2=CH-CH2O(CH2CH2O)12CH2-CH=CH2 compound (6):CH2=CH-CH2O (CH2CH2O)12CH3 [0023]

[Example 3] Compound (7)10g shown below was dissolved in about 500ml toluene / n-butyl alcohol (1/1) mixed solvent, the 86.67mg lithium hydroxide was added, it fully stirred, and the carboxyl group in a compound (7) was made to form into lithium carboxylate completely. Stirring mixture of compound (5)0.170g which removed the solvent after an appropriate time completely, and used it for it in 0.749g of obtained oily matter and the example 1, and the compound (6)0.081g was carried out, the ultrasonic wave was irradiated, and it was made to fully dissolve. After 2.47microl Adding a chloroplatinic-acid 6 hydrate (H2PtCl6.6H2O) isopropyl alcohol solution to this mixture 2% of the weight as a hydrosilylation catalyst, it slushed into the pan made from the Teflon of 3cm around, and when heated within the oven adjusted to 70 degrees C for 2 hours, the film with the transparent thickness of 0.3mm was obtained. After carrying out reduced pressure drying of this for two days at 70 degrees C furthermore, when ionic conductivity was measured, the value of 1.8x10-7 S-cm -1 was acquired at 25 degrees C. Moreover, when the same direct-current-voltage impression examination as an example 1 was performed, the current of 4.9microA continued for about two days. When the still more nearly same lithium cell as an example 1 was produced, early service capacity is 3.5 mAh/g and became 20 cycle eye with 2.9 mAh/g.

Compound (7): [Formula 5]



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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]
[Drawing 1] Drawing 1 is the cross section of the lithium cell of this invention.
[Drawing 2] Drawing 2 a shows a time change of the voltage by the charge and discharge under the constant current (3.77microA/cm2) of the lithium cell obtained in the example 1, and drawing 2 b shows time change of the voltage by the charge and discharge under the constant current (37.7microA/cm2) of the example 1 of comparison. In addition, in drawing 2 a and drawing 2 b, v is voltage, and t is elapsed time.
[Drawing 3] Drawing 3 a shows transition for every cycle of the service capacity by the charge and discharge under the constant current (3.77microA/cm2) of the lithium cell obtained in the example 1, and drawing 3 b shows transition for every cycle of the service capacity by the charge and discharge under the constant current (37.7microA/cm2) of the lithium cell of the example 1 of comparison. In addition, in drawing 3 a and drawing 3 b, D.C. is service capacity, and C.T. is the number of cycles. 1 -- the spacer made from Teflon, and 2 -- a nickel network and 3 -- a nickel network and 4 -- a positive electrode (lithium-manganese multiple oxide) and 5 -- a solid electrolyte and 6 -- a negative electrode (lithium foil) and 7 -- a nickel network (what stuck the lithium foil by pressure), and 8 -- a nickel network and 9 -- lead wire

[Translation done.]

* NOTICES *

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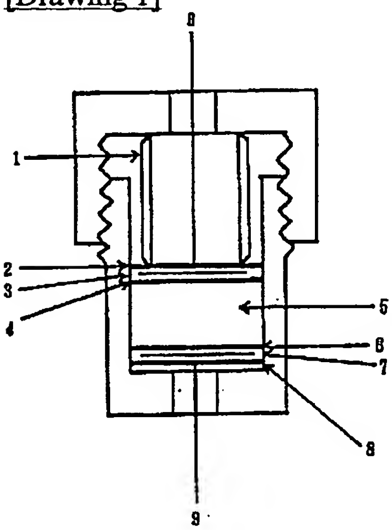
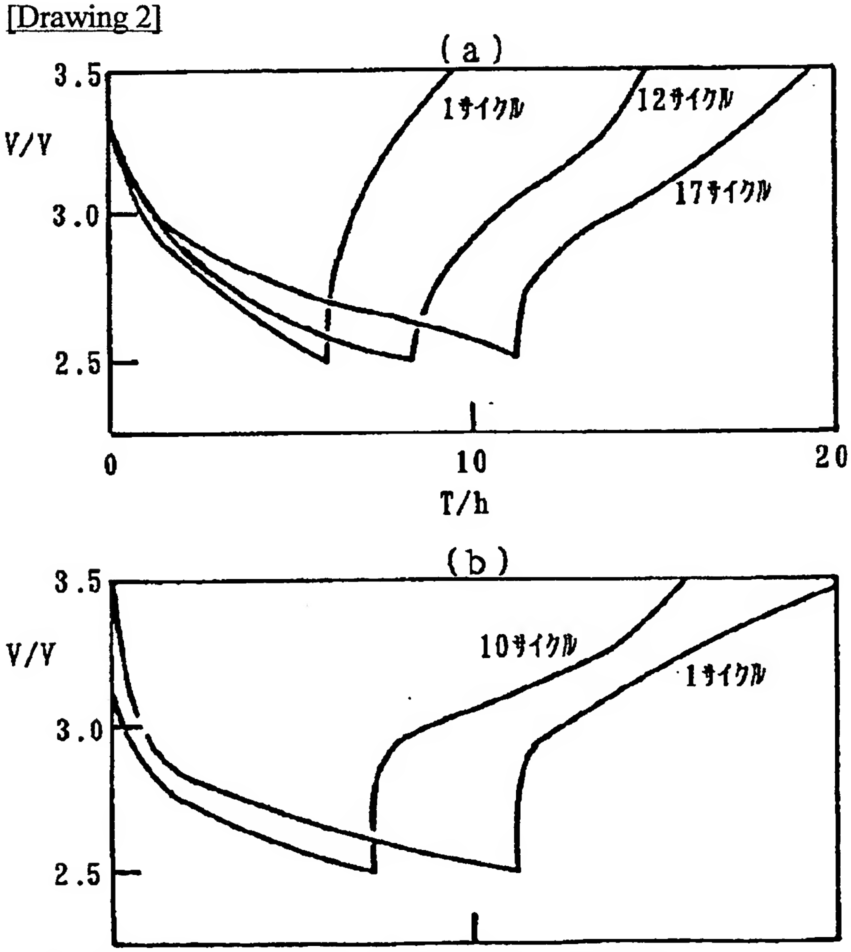
1.This document has been translated by computer. So the translation may not reflect the original precisely.
2.**** shows the word which can not be translated.
3.In the drawings, any words are not translated.

DRAWINGS

[Drawing 1]

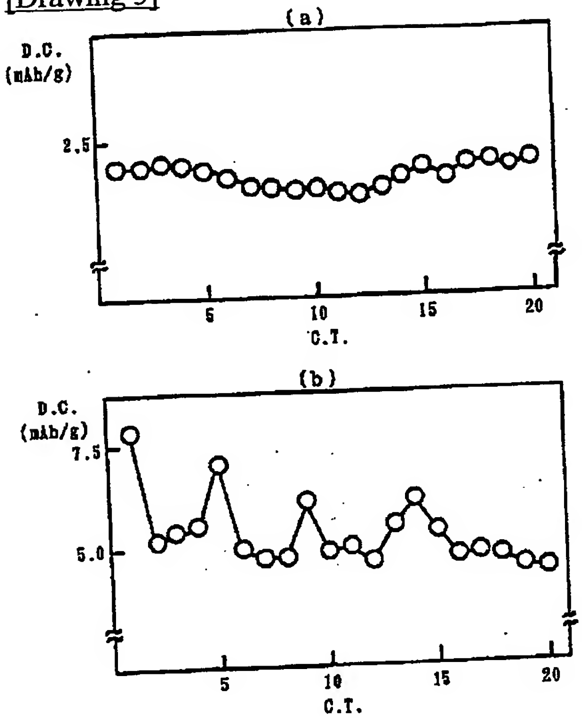


[Drawing 2]



0 1 2
T/h

[Drawing 3]



[Translation done.]